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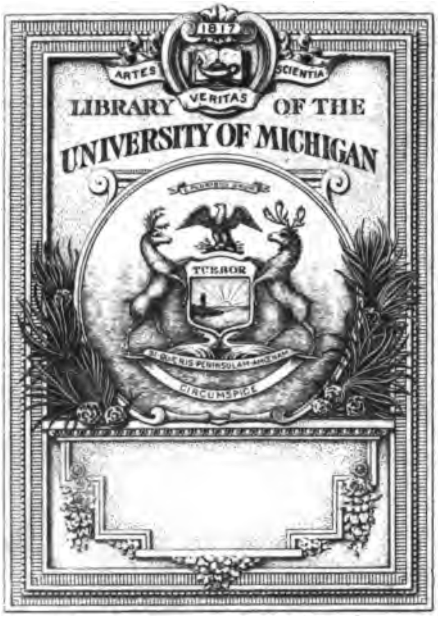

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COLLODION EMULSION.

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ON THE BROADS

Negatives taken with
Collodion Emulsion.

Collodion Emulsion

AND

ITS APPLICATIONS TO VARIOUS PHOTOGRAPHIC AND PHOTO-MECHANICAL PURPOSES, WITH SPECIAL REFERENCE TO TRICHROMATIC PROCESS WORK.

BY

HENRY OSCAR KLEIN.

LONDON:
PENROSE & CO., 109, FARRINGDON ROAD, E.C.
1905.

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PREFACE.

THIS little work has been written to serve the needs of the practical photographer, who has no time for experimental work, or for the sifting of scientific books to find working instructions, which have passed the test of time and have proved to be thoroughly practical. No others have been quoted.

Whilst the book chiefly deals with the application of Collodion Emulsion to Process Work, it is also hoped that it may be an introduction to other branches of applied photography, where Collodion Emulsion is not as well known as it deserves to be.

The Author, having been closely connected with Collodion Emulsion and its re-introduction into this country during the last six years, has had the opportunity of collecting information which, when now published in this book, may materially assist beginners over their initial difficulties. The credit of this re-introduction of Collodion Emulsion must rest with the firm of Penrose and Co., who, with self-sacrificing tenacity, have established Collodion Emulsion in this country, in face of very poor financial prospects.

I wish to acknowledge my indebtedness to Baron Von Hübl for his permission to quote extensively from his works on this subject, and to Mr. William Gamble for the revision of the manuscript.

HENRY O. KLEIN.

London, August, 1905.

INTRODUCTORY.

MOST photographers, in a general way, know how the wet collodion plate is prepared and used, although the process has now so largely gone out of use for ordinary photography, and in dealing with collodion emulsion, it will assist towards a better understanding of the subject if we recall some of the features of the old process, and trace the steps which led up to the introduction of emulsion processes.

The employment of collodion as a substratum for the silver haloid was first suggested by Gustav le Gray, in 1850, and was made known in a practicable form by Scott Archer in 1851.

Collodion (so named from the Greek word Κολλαω, to stick) is prepared by dissolving pyroxyline in a mixture of ether and alcohol.

Pyroxyline is cotton or linen which has been altered in composition by treatment with a mixture of nitric and sulphuric acids. The action of these acids is such that the cotton becomes soluble in various liquids, such as a mixture of ether and alcohol.

Cotton nitrated in this way is often inaccurately called gun-cotton, but, as a matter of fact, the nitration is stopped short of the production of gun-cotton. Pyroxyline is more soluble than the latter, and is also not so inflammable nor so explosive.

The collodion formed by dissolving pyroxyline in ether and alcohol is a transparent, glutinous liquid, which when poured on to the surface of a clean glass plate leaves, by the evaporation of the solvents, a beautifully uniform and highly transparent film, which adheres firmly to the glass.

In order to prepare the collodion to form a photographically sensitive surface, some soluble iodide or bromide salts, or a mixture of the two are dissolved in it, and the plate coated with this "salted" collodion is sensitized by being immersed, before the solvents have fully evaporated, in a bath of nitrate of silver. The silver nitrate reacts with the bromide or iodide in the film, and gives a layer of silver bromide or iodide on the surface of the collodion. The plate has to be exposed in a moist state.

If the plate were allowed to dry after being taken out of the bath, the silver nitrate upon the surface becoming concentrated by evaporation would crystallize, and in so doing would disintegrate or eat away the iodide of silver, producing transparent spots giving a freckled appearance to the film, which would be fatal to its photographic efficiency.

The inconvenience of having to use the collodion film in its wet state led to many attempts being made in the early days of photography, to prepare the film for use in a dry state. To obtain this condition, the excess of silver nitrate on the surface was removed by washing, but as this practically destroyed the sensitiveness of the plate, it was necessary to coat the surface of the film with some substance which will restore the sensitiveness. Such substances are technically known as "preservatives," because they preserve the sensitive surface from immediate contact with the air, very much in the same way as a varnish. This coating maintains the collodion in a porous condition, so that it may be acted upon by developers, which would otherwise fail to penetrate it.

The substances chosen for these preservatives were somewhat curious, consisting of tea, coffee, sugar, honey, albumen, beer, dextrine, gallic acid, tannin, etc. They, however, did something more than act as a preservative coating; they imparted an organic element to the sensitive film, forming what are known as organic sensitizers, their sensitizing action being due to their property of forming an organic compound of silver which greatly increases the sensitiveness of the plate, and, as a consequence, aids in giving density.

Collodion emulsion was a direct outcome of these collodion dry plate processes, and was probably suggested by experiments in connection with the latter. As far back as 1853, Gaudin proposed to use haloids in the form of emulsions, and in 1861, he gave details of his experiments. Three years later the first successful emulsion process was published by Bolton & Sayce, who used silver bromide emulsified in collodion, and from the principles they laid down all subsequent collodion emulsion processes have sprung.

Photographically, an emulsion may be described as a viscous fluid holding in suspension a sensitive silver salt in an extremely divided state, so fine indeed that when the film is spread on glass and viewed by transmitted light it shows no grain or structure, but presents a homogeneous appearance. It will thus be seen that where in the case of wet collodion the silver salt is on the surface, it is diffused throughout the film in the case of collodion emulsion.

A collodion emulsion used in its plain state can seldom be as sensitive as wet collodion, and never as sensitive under the most favourable circumstances as gelatine dry plates, except by colour sensitizing, but there are other qualities than sensitiveness required, and collodion emulsion will be found to possess advantages which are not possessed either by wet collodion or gelatine.

PART I.

THEORETICAL.

1.—THE CHEMICAL COMPOSITION OF COLLODION EMULSION.

THE actual preparation of collodion emulsion, suitable for colour sensitizing is difficult, requiring no small amount of chemical knowledge and special equipment. The collodion emulsion of commerce, however, is generally of a reliable nature, and it would hardly pay the practical man to spend valuable time in preparing emulsion himself. It is, however, desirable that he should know something of its constituents and their relative action.

To prepare a collodion emulsion, the silver haloid must be precipitated in the film itself, that is to say, we cannot satisfactorily prepare a silver haloid and add it to the plain collodion. We must bring together the silver nitrate and the haloid salt (usually a bromide), with which the silver re-acts, in the presence of one of the solvents in which collodion itself is soluble. Such a solvent is alcohol, and if we dissolve in it some haloid salt and mix this solution with the collodion, we can then add an alcoholic solution of silver nitrate also to the collodion, and thus precipitate the silver as a haloid in the required state of fine subdivision, so that it will remain suspended owing to the viscosity of the medium.

The chemistry of the process is very simple. By mixing the soluble bromide salt with nitrate of silver, we have formed a light-sensitive substance which is more sensitive than silver nitrate alone. This substance is bromide of silver, the re-action being

$$KBr + AgNO_3 = AgBr + KNO_3$$

Potassium Bromide + Silver Nitrate = Silver Bromide + Potassium Nitrate.

Something more is, however, required than this apparently simple process. Other chemical compounds are formed in excess, and these must be removed by washing the emulsion pellicle or the plate itself.

When the emulsion is washed before coating it is said to be a "washed" emulsion, and when the plates themselves are washed after coating, the emulsion is often described as "unwashed."

There are certain nitrates present, free ammonia, an excess of bromide salts, and silver nitrate. At the same time the large amount of water which has to be introduced on account of the insolubility of certain compounds in alcohol or ether must be removed. The emulsion is generally precipitated by introducing large quantities of distilled water and the after-treatment of washing the pellicle removes all water soluble substances.

The method of precipitation of the emulsion is now a question of importance. Collodion emulsion poured into water generally forms a large pellicle, which, being of a horny nature, keeps some of the water soluble salts preserved within the water-proof coat of collodion surrounding it. A better method is to pour a thin stream of emulsion into hot water. The alcohol and ether evaporates quickly and a fine precipitate is formed.

The usual way of forming the emulsion pellicle is to introduce small quantities of distilled water successively.

Plate II.

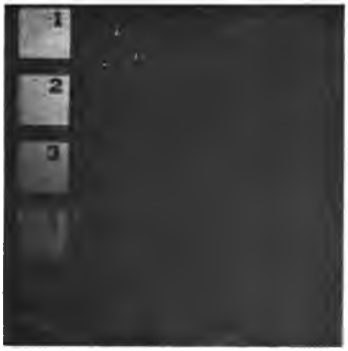

Fig. I.—Collodion Emulsion without Sensitizers.

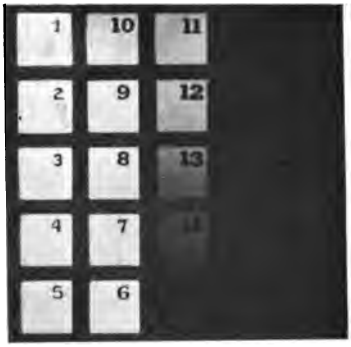

Fig. II.—Collodion Emulsion Sensitized with Eoside of Silver.

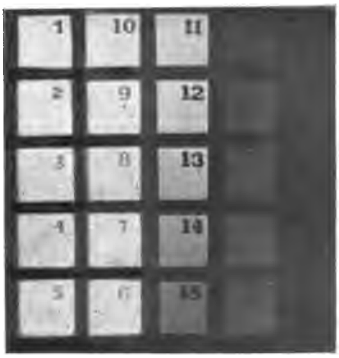

Fig. III.—Collodion Emulsion Sensitized with Ethyl Violet.

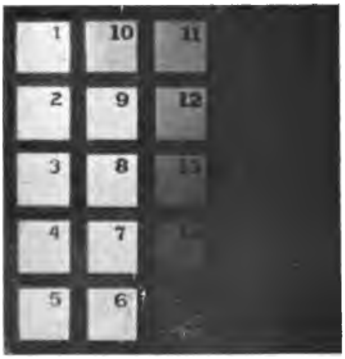

Fig. IV.—Collodion Emulsion Sensitized with Pinaverdol.

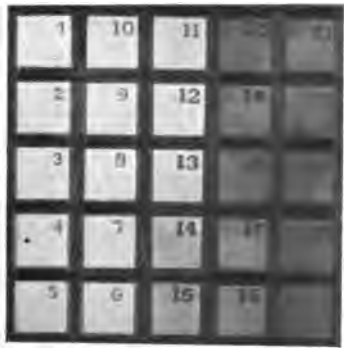

Fig. V.—Collodion Emulsion Sensitized with Ethyl Violet and Silver Nitrate.

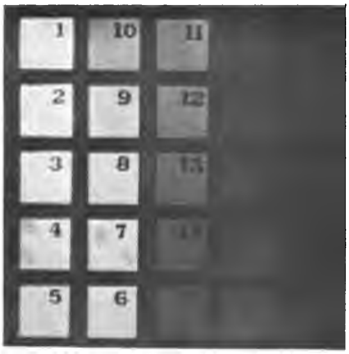

Fig. VI.—Lumière Panchromatic Dry Plate.

COMPARATIVE SPEED TESTS made with Chapman Jones' Sensitometer; Electric Incandescent Light, 5 c.p.; Exposure: 5 seconds; Developer: Hydroquinone.

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This forms a very fine sand-like precipitate which can be thoroughly washed in a very short time.

The sensitiveness of the emulsion is somewhat diminished by washing, but there is always a trace of free silver nitrate left in the film, to act as an extra sensitizer, and the sensitiveness is found to be sufficient for photographic purposes.

Plates prepared with such emulsions are of a rapidity generally below that of the ordinary wet collodion plate. (see Fig. I., facing page 15). Chemical and organic sensitizers, however, greatly increase the speed, and Fig. V., facing page 15, indicates a speed number which can only be equalled by a fast gelatine dry plate.

There only remains another kind of collodion emulsion to be mentioned, viz. :—that prepared with chloride of silver. Combinations of both chloride and bromide are also often met with, but as the simple chloride emulsions are only used for transparency work or for the coating of collodio-chloride papers, they will not be further discussed here.

The bromide salts generally used in the preparation of collodion emulsion are bromide of zinc and bromide of ammonium, both of which are soluble in alcohol. Bromide of potassium is not suitable for emulsions, in consequence of its total insolubility in alcohol. Chlorides are also added to emulsions for the purpose of eliminating free silver, but this tends to somewhat decrease sensitiveness. Chloride of cobalt has been used for this purpose, but Von Hübl considers that the cheaper chloride of zinc will do equally well.

Collodion emulsion which contains an excess of silver nitrate will not resist the action of strong developers. Bromide and other substances must therefore be added to the developer to prevent veiling.

It should, however, be remarked that veiling or blackening may be due to exposure of the emulsion to actinic light. With an emulsion of bromide of silver, prepared in actinic light, whether the silver or the bromide was in excess, it will become instantly blackened, even by a weak developer, whilst the bromide of silver itself, diffused in the collodion undergoes no visible change and only blackens after a long exposure to light.

The methods employed in making collodion emulsion chiefly govern the sensitiveness of the preparation. Collodion emulsions showing excess of bromide salts are about one-fifth of the speed of wet collodion, whereas emulsions prepared with silver oxide of ammonia or with silver nitrate in excess are considerably faster. The process of ripening the emulsion also greatly increases the rapidity. In this process of ripening the bromide of silver particles increase in size.

Baron Hübl states that the size of the bromide of silver particles at the time of production measure from 0·0005 to 0·001 millimetres and after the process of ripening increase from 0·002 to 0·005 millimetres.

The colour of the emulsion when examined by transmitted light determines its characteristics. Emulsions which contain finely-divided bromide of silver, and which by transmitted light seem orange red in colour, resist the developer better, and have less tendency to produce veil than those with coarse grained bromide of silver. This is easy to observe if, after allowing the emulsion to stand a long time, the top and bottom part are comparatively tested. The top part contains finely divided bromide of silver and gives clear glass negatives, whilst it possesses less sensitiveness to light than the bottom part, containing the coarse-grained bromide of silver, and which by transmitted light has a blue-grey appearance.

2.—INCREASING OF SENSITIVENESS BY MEANS OF ORGANIC AND CHEMICAL SENSITIZERS.

We have already mentioned that a great many organic substances have been used to increase the sensitiveness of collodion emulsion, such as beer, tea, coffee, sugar, dextrine, gum arabic, etc., but the active agent in most cases was found to be the alkali which those substances contained.

We must further mention Narcotine and Codeine as good sensitizers, and, most important of all, silver nitrate and certain aniline dyes.

Silver nitrate is a bromine-absorber and this chemical sensitizer, as well as other halogen absorbers, is of great importance. The sensitizers now generally in use are formed by certain aniline dyes and their compounds with silver nitrate, and isochromatic photography is indebted to Dr. E. Albert, of Munich, who was the first to prepare colour-sensitive collodion emulsions of high rapidity, by introducing eoside of silver into the emulsion. The organic sensitizers are only of value in collodion emulsions which are to be used for transparency, opal, and lantern-slide work, whereas the chemical and the optical or colour-sensitizers are chiefly made use of in process work, and for three-colour portrait and landscape work where orthochromatism and great rapidity are requisite.

3.—SENSITIZING OF COLLODION EMULSION FOR ISOLATED PARTS OF THE SPECTRUM.

Collodion emulsion can be sensitized for nearly all colours of the spectrum, without losing its general sensitiveness, which as a rule is greatly increased by the addition of aniline dyes.

The colour-sensitizing of collodion emulsion can be accomplished with greater accuracy than with gelatine dry plates, a phenomenon which has been investigated by Baron Hübl, who stated that the screening defect of gelatine plates, caused by the quick absorption of a dye, is so great that a complete shifting of the region of sensitiveness takes place, which makes the accurate adjustment of the colour-sensitiveness of a dry plate an extremely difficult and uncertain process. Collodion emulsion is almost free from this defect, the film does not stain very intensely and the bromide of silver particle, which it is our object to colour, is not embedded in a deeply coloured medium, forming in itself a very efficient, but undesirable light filter. The aniline dyes generally in use for orthochromatizing collodion emulsion are the Eosines, Acridine, Uranine, Thiazol Yellow, Erythrosine, Rose Bengal, Cyanine, Ethyl Violet, Nigrosine, Chlorophyll, Wool-black, Diamant Black, Pinaverdol, Homocol and Mono-bromo-fluorescinate of Sodium.

These dyes may be used either singly or in combination, but in the latter case their chemical composition should be of a somewhat similar nature. This subject has been very elaborately treated by Baron Hübl, in his work, "Three-Colour Photography," in which he says :—

"The ordinary photographic plate is generally called blue sensitive, because a moderate exposure shows after development only a visible action of the blue and violet spectral rays on the photographic plate. If this exposure is prolonged, the green, then the yellow, and finally, also the red rays exert a chemical action. A photograph of the spectrum extends with short exposure to line F, but by prolonged exposure widens the band towards the red, especially in gelatine dry plates.

"The most powerful action is due to the spectral violet, but the gelatine plate is of greater blue sensitiveness than the collodion emulsion. Daylight contains only a small amount of ultra violet rays, the glass of the lens or the filter absorbs a great deal of the same, and the high sensitiveness of the bromide of silver does not extend very far into the ultra violet. These rays are therefore without influence on the photographic action of the pigments."

The addition of suitable dyes to the bromide of silver greatly increases the sensitiveness of the least refrangible part of the spectrum, and spectrographs show, besides the characteristic band in the blue violet, another band of sensitiveness in a part of the spectrum nearer the red.

The bromide of silver plate can be sensitized for green, yellow and red in such a high degree that pigments reflecting such rays will be rendered in the photographic print more or less light with even exposures of short duration.

Not every dye, however, acts as a sensitizer, and amongst a great number which have been tested spectroscopically many show a band of sensitiveness, but in only a few cases is the band sufficiently pronounced to be of practical photographic use. The sensitizing by means of a dye can only take place if the dye itself, or in combination with the bromide of silver, is light-sensitive, and, further, if the dye combines with the particles of bromide of silver and colours same. The photographic film will then be made sensitive for light of a certain colour and according to Dr. H. W. Vogel's law of absorption for those rays which the coloured bromide of silver absorbs.

Baron Hübl further considers the following conditions as essential :—

"*a*. The dye must readily decompose by the action of light.

The bromide of silver is not influenced only by the blue rays, but also by the less refrangible ones, provided the exposure is long enough. If we expose an emulsion film sensitized with cyanine to rays of different colour, we find that the dye as well as the bromide of silver is altered : the first by the action of the orange yellow rays, the latter by the influence of the blue rays, the orange yellow rays being the absorbed ones. The molecular composition will be destroyed and the new compound will be formed by the altered position of the atoms.

We know that bromide of silver shows a tendency to decompose when exposed to yellow light, therefore the addition of a dye which readily decomposes will only help to strengthen this tendency and bring about an active decomposition.

The bromide of silver will be directly influenced by the blue rays and by the orange indirectly through the agency of the cyanine, the degree of this influence being high enough to permit a reduction of metallic silver whenever reducing agents are applied.

b. The dye must colour the bromide of silver.

If the dye only colours the collodion, without imparting colour to the bromide of silver particle, no sensitizing action will be noticeable. The dye molecules are actually separated from the bromide of silver molecule, and they cannot influence each other.

If bromide of silver sensitized with a quickly fading dye is exposed to daylight, a change in appearance will be quickly visible. The dye bleaches and the bromide of silver shows a grey colour.

Dr. Eder states in his "Handbook of Photography" that the decomposition of a dye not only increases the tendency of bromide of silver to decomposition, but that the latter also increases that of the dye.

The presence of a soluble bromide salt or of silver nitrate, however, often prevents the colouring of the bromide of silver grains, and no sensitizing action can be recorded.

The presence of a soluble bromide prevents the cyanine from colouring the bromide of silver, and this furnishes an explanation why emulsions made with bromide in excess cannot be sensitized with cyanine, although they may have been prepared with silver oxide of ammonia or may contain chemical sensitizers.

This sensitiveness can, however, be restored by the addition of a trace of nitrate of silver, sufficient to do away with the excess of bromide.

If on the other hand the silver is in excess, the sensitizing action of the cyanine again disappears."

Another interesting point is the following:—

The compounds which are formed by the bromide of silver and the dyes do not quite conform with the rule of showing a sensitiveness for those rays which the dye solution absorbs. Hübl states that this phenomenon, which apparently contradicts Vogel's theory, but in reality actually confirms it, is due to the fact that a dye shows a different shade of colour in different solvents. Eosine, for instance, imparts different colours to alcohol and to water, whilst if dried on paper or glass it shows a still different colour. A dye only acts as a sensitizer if the dye colours the bromide of silver, and the colour of the bromide of silver will govern its sensitiveness for particular kinds of spectral rays. The alcoholic solution of eosine is yellowish red and absorbs the green rays. Bromide of silver coloured with eosine, however, is violet red, absorbs the yellow green rays, for which it is also sensitive. All dyes sensitize, therefore, more towards the red end of the spectrum than we should expect from the spectroscopic examination of the alcoholic dye solution.

The intensity of light also plays an important part in orthochromatic photography.

Hübl states "that there exists a minimum of light intensity for every light sensitive substance, below which they fail to be influenced by the action of light. This intensity is generally supposed to be higher for dyes than for bromide of silver, which explains that when the illumination is of low intensity we may obtain a fully exposed negative, without, however, the isochromatic rendering, supposed to be given by the sensitizer. The more intense the illumination the more active the dye. The best illumination is therefore sunlight."

The influence of dye excess must also be considered. The bromide of silver can only absorb a certain amount of dye and an excess will only colour the medium, in this case the collodion, and the rays of light will have to penetrate this coloured collodion which acts as a light filter. This light filter, absorbing the very rays of light for which the dye made the bromide of silver sensitive, will be exceedingly detrimental to the speed of the plate. We find a good example in a collodion emulsion sensitized with ethyl violet. Now ethyl violet, if examined spectroscopically, absorbs orange and it also sensitizes collodion emulsion for orange. A collodion emulsion sensitized with this dye shows an intense purple colouration and a low speed similar to Fig. I., facing page 15. If the plate is washed before exposure the sensitiveness of the plate is very much increased (*vide* Fig. III., facing page 15). We simply weaken the absorption of the collodion, which besides the bromide of silver has also been stained with the deep violet dye. Pinaverdol, Diamant Black, and Homocol all need good washing before exposure.

Up to the present there is still wanting a dye which will make collodion emulsion truly panchromatic, *i.e.*, impart equal sensitiveness for all colours of the spectrum. A combination of Diamant black P.V. of the firm of Bayer and Co., Elberfeld, with Uranine and Erythrosine has, however, given a collodion emulsion plate which shows very high general sensitiveness, and relatively panchromatic qualities.

For most purposes it will be advisable to colour-sensitize the emulsion for isolated parts of the spectrum, and to correct and modify the curves of sensitiveness by means of suitable light filters. The illustrations, facing page 23, indicate the curves of sensitiveness of the most usual aniline sensitizers. The reading was taken of normal spectrograms, Rowland's diffraction grating in Tallent's spectroscopic camera being used. Illustrations facing page 15 show tests made with Chapman Jones' sensitometer and give a fair idea of the high speed which collodion emulsion can occasionally attain.

4.—THE CHEMICAL COMPOSITION OF COLOUR SENSITIZERS.

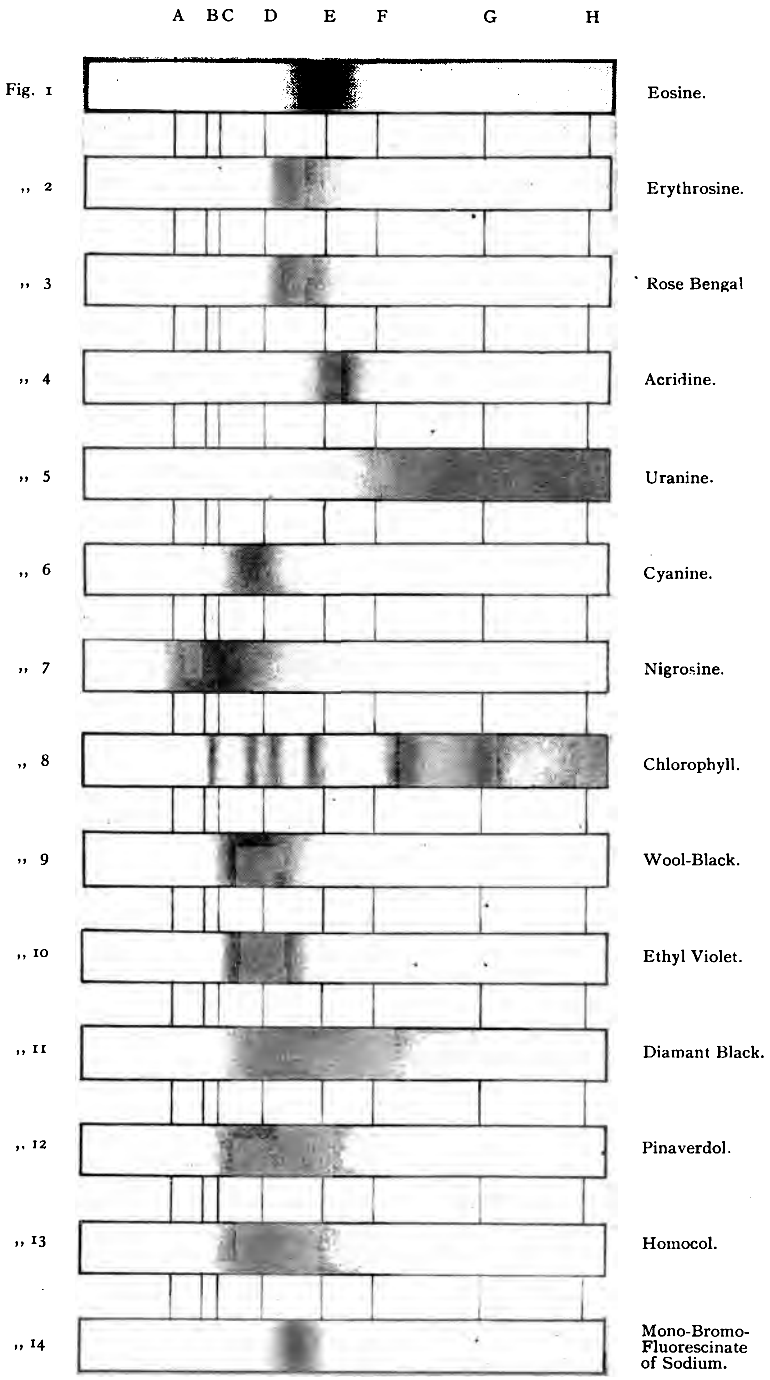
THEIR SUITABILITY AND SELECTION.

(1) Eosine Yellow is the potassium derivative of Tetra-bromo-fluorescin, and is soluble in water or alcohol, showing an absorption spectrum as Fig. I.

Collodion emulsion sensitized with Eosine is, therefore, sensitive for yellow green. It is greatly used as a sensitizer.

(2) Erythrosine is the sodium salt of Tetra-iodo-fluorescin, is soluble in water and alcohol, and sensitizes collodion emulsion for green. The absorption spectrum is shown in Fig. 2.

Plate III.



ABSORPTIONS OF DYES.

(3) Rose Bengal is the potassium Tetra-iodo-chloro-fluorescin, and is soluble in water and alcohol, sensitizing collodion emulsion for yellow and green, as Fig. 3 shows.

(4) Acridine is an orange yellow aniline dye, is soluble in alcohol, and used as a sensitizer for green. The absorption spectrum is shown in Fig. 4.

(5) Uranine is a sodium salt of fluorescin (Tetra-oxy-phtalo-pheno-anhydrid), is soluble in water and alcohol. Good sensitizer for green. Absorption spectrum Fig. 5.

(6) Cyanine is prepared from Chinolin, and forms crystals of metallic lustre. Soluble in alcohol. Commercially obtainable cyanine is an iodine compound, forming with nitrate of silver iodide of silver, which is an undesirable silver compound in rapid emulsions. Chlorocyanine must be used, which producers good yellow and orange sensitiveness. Fig. 6.

(7) Nigrosine, a black powder, soluble in alcohol and water, is the sodium derivative of induline sulphur acids. Sensitizes emulsions for red, as shown in Fig. 7.

(8) Chlorophyll can be extracted by immersing ivy leaves or other evergreen leaves in alcohol. It sensitizes collodion emulsion for red, and is a good, but very unreliable, sensitizer. Fig. 8.

(9) Wool-black 6B, an azo dye stuff, is a black powder soluble in alcohol, and a very good sensitizer for orange, especially if weak silver bath is used.

The absorption spectrum is shown in Fig. 9.

(10) Ethyl Violet is the hydro-chlorate of Hexa-Para-Rosaniline, is soluble in water and alcohol, sensitizes collodion emulsion for yellow and orange. First introduced by Prof. Valenta. Absorption spectrum, Fig. 10.

(11) Diamant Black, P.V., an azo dye, is a black powder, soluble in alcohol with deep red colour. First introduced by the author as a sensitizer for orange and

red. If combined with Uranine and Erythrosine almost panchromatic emulsions of high rapidity can be prepared Absorption spectrum, Fig. 11.

(12) PINAVERDOL is one of the Iso Cyanine dyes, gives exceedingly clear working emulsions of a good green and slight orange sensitiveness, but of a rather low speed number. Fig. 12 shows its absorption band.

(13) HOMOCOL probably of a similar chemical composition as Pinaverdol, and in its action much the same. It was introduced by " The Bayer Co.," and is a very useful dye, if clear working emulsions of good colour sensitiveness, but moderate speed, are required. Fig. 13.

(14) MONO-BROMO-FLUORESCINATE OF SODIUM, first intrduced by Dr. Eder. The name indicates its composition. Excellent sensitizer for green, of high speed if used with a ½ per cent. silver bath. Fig. 14.

CANARY II., used as a sensitizer for the yellow printing plate in three-colour work, soluble in water or alcohol.

Most of the above dyes can be tested in a 1 : 500 alcoholic solution, as to their suitability as colour-sensitizers. The proportion for mixing with the emulsion varies very considerably.

In addition to the list of aniline dyes, which up to the time of writing have been found suitable for colour-sensitizing of collodion emulsion, we have to record the various colour-sensitizing compounds of commerce.

SENSITIZER " A " introduced by Dr. E. Albert is an eosine silver compound containing picrate of ammonia and glycerine. Can be mixed with emulsion in proportion 1 : 10 or an alcoholic diluted solution can be flowed over the plate. Excellent sensitizer for yellow green.

SENSITIZER R.P. Rose bengal or rhodamine silver compound, containing glycerine and picrate of ammonia. Good sensitizer for orange and yellow.

SENSITIZERS " AA " " RR," " GG." Aniline silver compounds introduced by Dr. E. Albert as sensitizers for three-colour work.

Their actual composition is a trade secret, but comparative experiments proved " AA " to give same speed and colour rendering as " A " sensitizer, which has probably been renamed for convenience sake.

SENSITIZER " RR " is, if compared with ethyl violet, inferior in speed and colour rendering.

SENSITIZER " GG " used for the yellow printer has to be exposed behind a blue-violet filter and is certainly much slower than "A" sensitizer, under similar conditions.

The firms of Messrs. Brendamour and Klimsch also bring colour sensitizers on the market, and although their composition is unknown, we may assume them to be very similar to those of Dr. E. Albert. Comparative tests have shown great resemblance.

NEW SENSITIZER " C." Excellent colour sensitizer for orange and red. Based upon ethyl purple. First introduced by Messrs. Penrose & Co.

This sensitizer can be mixed with the emulsion or can be diluted with alcohol and flowed over the plate, which is generally washed before exposure.

OLD SENSITIZER " C," introduced by the author. A cyanine silver compound, containing glycerine. Good sensitizer for orange and red in three-colour work. Recipe given on page 52.

This sensitizer is not commercially obtainable and has been abandoned on account of the difficulties experienced in every-day commercial work. In the hands of careful workers, it shows many excellent qualities.

The selection of aniline dyes for sensitizing purposes, amongst the many hundreds which are now commercially obtainable, takes up a good deal of time, because ocular spectroscopic tests are of little value and spectrographic tests are always requisite. Dr. Vogel's maxim, that an aniline dye sensitizes for that part of the spectrum which the dye absorbs, is a great help in our experimental work, but there are a great many dyes showing absorption bands, yet producing no sensitizing action if mixed with emulsions. We are therefore bound to fall back upon practical work with the spectroscope and the camera.

Although a spectroscope attached to a camera in place of the lens provides an excellent apparatus for the testing of aniline dyes, it is preferable to use diffraction gratings, on account of the spectral zones being of more even distribution and more widely dispersed. An excellent little instrument permitting ocular and spectrographic tests is Tallent's Spectroscopic camera.

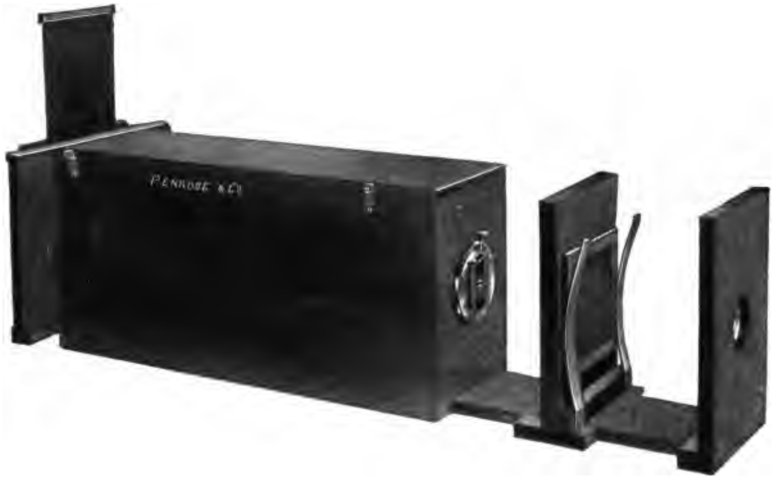
The following description of this useful instrument is taken from a booklet issued by Messrs. Penrose & Co., the makers :—

> " A box, forming a camera, has a dark slide at one end. At the other end, and outside the box, is a narrow slit of short length, D. This is at the principal focus of the lens, E, which is of short focus. Rays from the slit fall, after refraction by the lens, parallel on to the prism-grating, F, where each ray is dispersed into its constituent rays. All rays of the same colour emerge parallel, and, falling on the lens, G, are brought to a focus at its principal focus in the plane of the ground-glass or sensitive plate, C." (See Plate IV.)

The camera has a dark slide which permits 4 or 5 exposures being made on a ¼-plate.

Chemically clean glass plates are coated with emulsion and an alcoholic solution, about 1 : 500, of the dye which is to be tested is poured over the plate, which is immersed for two minutes in a ½% nitrate of silver bath. All operations should be performed as much as possible in darkness, although the absorption band of the dye, visible when spectroscopically examining the alcoholic solution in a glass tank, will indicate whether green or red light can be used in the dark-room.

Plate IV.



Tallent's Spectroscopic Camera.

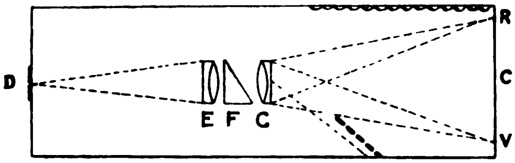
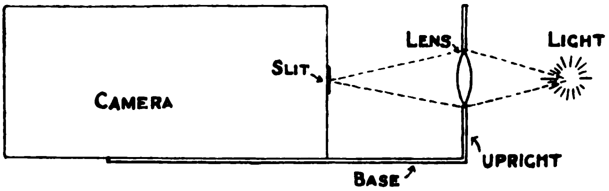


Diagram of the Spectroscopic Camera.



Method of Illuminating the Slit by Artificial Light.

If a dye, for instance, shows a strong absorption band in the orange, red light in the dark-room cannot be used, as the emulsion containing the dye may be orange sensitive. A green light will have to be used in such a case.

In combining two or more dyes to form colour-sensitizers, we must see that their chemical composition is not too widely different, and that their sensitizing action is of somewhat similar intensity.

We shall have particularly to guard against an excess of dye in the emulsion, which, as pointed out in the previous chapter, is absolutely fatal to the sensitizing action of the dye. In many cases the plates will have to be thoroughly washed before exposure.

Another very useful instrument for this kind of work is Chapman Jones' sensitometer, although the illuminant, the standard candle, is not quite a suitable source of light. Wherever possible, reflected arc light should be employed. Finally, it will be found of greatest value to make test exposures on a good colour chart. The spectrum as well as sensitometers often furnish very different results to those obtained from a colour chart, and the practical worker, dealing chiefly with reflected coloured light which is of a more even intensity through all the range of colours than that of the spectrum, should place his greatest reliance on the tests with the colour chart. Correct exposures must be given, and white paper should be rendered with the same density in all the test exposures.

The practical worker, however, will rarely be able to spend the time necessary to conduct such experimental work, fascinating as it may be, but it will well repay him to carefully read the reports of scientific institutions, and in particular those of the Imperial High School of the Graphic Arts in Vienna, translations of which are always given in English technical journals, as scores of aniline dyes are constantly tested at this Institute in regard to their suitability as colour sensitizers.

5.—THE ELEMENTARY PRINCIPLES OF TRICHROMATIC WORK.

Although three-colour work has given life to the almost extinct process of collodion emulsion, it is not within the province of this little book to go deeply into the subject, and we propose to only acquaint the reader with certain terms which may be used, and to briefly outline the process.

The source of all colour is light. If a ray of sunlight, for instance, passes through a prism, it will be refracted and will undergo a similar decomposition to that produced when it passes through drops of water, and forms the well-known rainbow colours. We note that white light is composed of many coloured lights, ranging from deep violet, through blue, green, yellow and orange to red. If any one of these components is taken away or absorbed by means of a light filter, the remainder which passes is no longer white but coloured light, because some of the constituents of white light are missing.

If we view a series of colours in the red light of our dark-room, *e.g.*, if we illuminate a colour chart with light, which is deficient of all other rays except the red, which is, in other words, a monochromatic light, we note that all the colours are monochromes over which the red light is spread. As colour is supposed to be non-existent, nothing material, only an internal sensation which our nerves of vision convey to our brain, it is conditioned by the source of light and by the properties of the coloured surface for absorbing or reflecting certain components of white light. A sheet of black velvet, in whatever light viewed will be black, because the material absorbs all species of rays which constitute white light. None will reach our retina, and therefore the object appears black. White paper absorbs none, but reflects all rays and so gives the same colour-impression as white light. A green leaf absorbs all coloured rays, except the green, which are reflected into our eye and so cause the sensation of green light.

Now, it has been found that by using a blue-violet, a green and a red light filter any coloured object can be so decomposed into three monochromes that they represent the exact amount of yellow, red and blue necessary for the re-composition of all colours in nature.

Yellow, red and blue will reproduce all pigmentary colours, and if the exact proportions of the one to the other can be photographically obtained, we can by superposing the three positives which are stained in their respective colours, obtain a true reproduction of the coloured object.

The appliances necessary beside those which most photographers already possess, are the light filters, which, in the case of a so-called panchromatic emulsion, are blue-violet, green and red.

As a truly panchromatic emulsion of high speed is not known, we find it necessary to colour-sensitize the collodion emulsion for certain parts of the spectrum, and correct the inaccuracies of the colour-sensitiveness by means of correction light filters.

The filters generally used for collodion emulsion tri-chromatic work are much too deep in colour, or in other words, their absorption bands do not complement, but overlap too much the regions of insensitiveness of the plate which we employ. The standard colours of a deep blue-violet, green and red are still in the mind of the practical man, and he will still endeavour to view his original through the filters and find by ocular observation whether they are correct or not. Such methods, although not scientific, may have been of use in tri-chromatic dry plate work; they are more than useless where collodion emulsion is concerned, as we meet with well-defined bands of sensitiveness, and it is possible to calculate upon the insensitiveness of the plate for certain spectral zones.

Collodion emulsion sensitized with eoside of silver in the presence of picrate of ammonia is so insensitive to orange and red that it would serve no purpose to absorb the orange or red by means of a dark-green filter. The filter in this case is of a light-yellow colour, and even without a filter a good red printing plate can be made. This may be explained by the action of the picric acid, which effectively absorbs the blue-violet and the blue.

Again, if we sensitize collodion emulsion with ethyl violet, an emulsion which everybody knows can be handled with safety in green light, why should we absorb this green by means of a filter, if our emulsion is not sensitive to it, when, by doing so, we only increase the length of our exposures.

Here again I warn my readers against the practice of using the spectrum as an infallible test object when adjusting our filters. Let the spectroscopic tests support your practical colour chart tests, but do not do without the latter for practical work. Once a correct colour rendering seems to have been accomplished, the negatives should be printed as three-colour transparencies to assure ourselves of the correctness of colour rendering, and those monochrome negatives should be kept as standards to be compared with the chart, which is to be photographed with the object.

Another mistake which is met with often is that the experimenter discovers that a certain broader absorption-band in his filter renders one particular colour more to his liking, without, however, noticing that by doing so two others are rendered disproportionately incorrect. The most abused filter in three-colour work is, I believe, the green sensation or red printing filter.

Not that this particular filter ever made itself prominent by a bad colour rendering, this fault is rarely met with, but this filter is part of a process which, as Hübl says, we are most unfamiliar with and which seems to the practical man the most important of all. If blue or red predominates in the finished print, we promptly blame the incorrect colour separation caused by the filters.

" We generally hear complaints about the red printing plate, which spoils all the greens and violets and shows a red tint predominating over all the picture.

Those who do not know the theory of three-colour photography find the cause of this trouble in the imperfections of the red printing plate. After reducing the red print, which does not help matters, the negative is intensified, which only makes things worse, and then the filter is made of a darker green colour. A new impression shows no improvement, and there is only one way left open, retouching. The cause of the difficulty may, however, not rest in the negative at all.

If the green is spoiled by the red impressions the yellows and blue are so impure that they do not stand the addition of the red. If we choose in the place of the so-called pure blue a green-blue we find the red impression harmless, or even necessary, to produce certain green shades in the original.

We come finally to the conclusion that the correct photographic decomposition is not so difficult to obtain, but that one of the chief causes of the " Filter trouble " lies in the impurity of our printing inks. The best proof for this can be found in the three-colour transparency, which is not materially influenced by slight differences in the adjustment of the light filters or the sensitiveness of the plate."

Correction light filters for collodion emulsion trichromatic work are now commercially obtainable, and instructions as to the making of same can be found in the various text books on the three-colour process.

6.—CHEMICAL CHANGES IN COLLODION EMULSION NEGATIVE MAKING.

Chemical composition takes place when two or more bodies so unite as to form a compound body, which differs in its properties from its components. This clearly defines the difference between mechanical mixture and chemical combination. Chemical composition is governed by the laws of affinity, which attracts atoms of various substances and so produces new bodies.

To make the various operations, connected with the production of a negative better understood and to enable the practical worker to account for his actions, we propose to explain the most important chemical changes.

The collodion emulsion film consists of bromide of silver ($AgBr$) in the vehicle of collodion, which is an organic compound. When exposed in the camera, the light changes those molecules of bromide of silver which are exposed to it into silver sub-bromide (Ag_2Br), liberating bromine (Br).

$$2\,AgBr + \text{light} = Ag_2Br + Br$$

A developing compound, for instance, hydroquinone ($C_6H_4(OH)_2$) reduces the newly formed silver sub-bromide (Ag_2Br) into metallic silver (Ag).

$$2Ag_2Br + C_6H_4(OH)_2 = Ag_4 + C_6H_4O_2 + 2HBr.$$

The unaltered bromide of silver ($AgBr$), constituting the deepest shadows of our negative is dissolved by the hyposulphite of sodium ($Na_2S_2O_3$), which latter must be in excess so as to produce a water-soluble substance ($Ag_2S_2O_32Na_2S_2O_3$).

$$\begin{gathered}2AgBr + 3Na_2(S_2O_3) = Ag_2(S_2O_3)\\ 2Na_2(S_2O_3) + 2NaBr\end{gathered}$$

The negative now consists of finely divided metallic silver (Ag) embedded in the collodion film.

Intensification with mercury ($HgCl_2$) produces a substance known as calomel (Hg_2Cl_2)

$$2Ag + 2HgCl_2 = Hg_2Cl_2 + 2AgCl$$

To blacken the bleached image we apply ammonia (NH_4OH)

$$\begin{gathered}2Hg_2Cl._2 + 4(NH_4)OH = Hg_2O + Hg_2\\ Cl(NH_2Cl) + 3NH_4Cl + 3H_2O.\end{gathered}$$

Intensification with copper may be needed, in which case the metallic silver is converted into silver bromide ($AgBr$) and copper bromide ($CuBr$).

$$Ag + CuBr_2 = AgBr + CuBr$$

The negative is "blackened" with nitrate of silver ($AgNO_3$) producing copper nitrate $(CuNO_3)_2$

$$CuBr + 2AgNO_3 = Cu(NO_3)_2 + Ag_2Br$$

Copper bromide is slightly soluble in water. The negatives must therefore be washed for a short time only, so as not to injure density.

We may further wish to apply iodine (I), and reduce or "cut" with cyanide of potassium (KCN) in which the iodide of silver (AgI) dissolves.

$$Ag + I = AgI$$
$$AgI + 2KCN = AgKCN + KI$$

Or the image consisting of iodide of silver (AgI) is treated with Schlippe's Salt, Na_2SSbS_5, forming Ag_2SSbS_5, an intense orange coloured substance.

$$2AgI + Na_2SSbS_5 = Ag_2SSbS_5 + 2NaI$$

In the case of lead intensification, the negative is converted into $Ag_4FeC_6N_6$ and

$$6Pb_2\ FeC_6N_6$$

Silver + ferridcyanide of potassium + nitrate of lead

$$4Ag + 4K_3FeC_6N_6 + 6Pb(NO_3)_2 =$$
$$Ag_4FeC_6N_6 + 3Pb_2FeC_6N_6 +$$
$$12KNo_3$$

7.—DARK-ROOM ILLUMINATION.

If collodion emulsion is used without the addition of colour-sensitizers, orange dark-room light is perfectly safe, but if colour-sensitizers are added, the light will have to be a monochromatic red or green, according to the sensitiveness of the emulsion.

But at all times excess of dark-room light should be avoided. A simple way of ascertaining whether the dark-room light is safe, is the following. Coat a plate with emulsion, colour-sensitize and place in the dark slide.

Draw one half of the shutter and expose the thus unprotected other half of the plate to the dark-room light for a minute or two, and develop. Although so-called " Safe-lights " are on the market, and it is perhaps best to purchase a reliable light-filter, a few hints as to the preparation of such safe-lights may be useful.

ORANGE LIGHT FILTER.

Take an unexposed dry plate, fix it and wash under the tap for about half an hour, then immerse in an aqueous solution of aurantia and brilliant yellow and stain the film until, spectroscopically examined, the whole of the violet and blue are absorbed. Stand up to dry.

RED LIGHT FILTER.

Stain two plates with rhodamine and brilliant yellow respectively.

The brilliant yellow is to absorb all the violet and blue, the rhodamine all the blue-green and the green. If the two plates are bound together, nothing but pure red will pass, as an examination with the spectroscope will show.

GREEN LIGHT FILTER.

The dyes used are naphthol green and auramine and methylene blue. Gelatine-coated plates are stained and superposed. If a brighter light is required, brilliant green and auramine or methyl blue and auramine are recommended, but with the latter it is difficult to absorb the entire red end of the spectrum. If spectroscopically examined, this light is to pass pure green only. It is advisable to examine against a very powerful light, as certain rays in the violet are often unabsorbed by the filter and still remain undetected on account of their poor luminosity. For spectroscopic tests, comparison camera spectroscopes are to be recommended.

The dye solutions are best made in concentrated stock, well filtered through filter paper and diluted when required. A small quantity of alcohol can be added to facilitate the drying of the filter.

PART II.

PRACTICAL WORK.

1.—COLLODION EMULSION WITHOUT COLOUR SENSITIZERS.

GENERALLY speaking collodion emulsion may be used for every kind of photographic work for which wet collodion or gelatine dry plates have hitherto been used. The treatment and method of handling will differ according to the purpose to which it is applied. We accordingly set forth the different processes, commencing with the oldest and simplest applications, such as to ferrotype plates, wood blocks, leading up to the more complex negative making processes in which colour-sensitizers are introduced into the emulsion. First, however, we deal with the preparation of the glass plates.

Only new glass should be used, as scratches show in the negative. *Vide* Fig. II., following page 80.

The plates should be immersed in a strong caustic potash solution, if they are old negatives, so as to free the glass of the film. If they are new glass plates, immerse them for a few hours in

Bichromate of potassium	2 ozs.
Sulphuric acid	3 „
Water	25 „

Rinse under the tap and polish with an alcoholic solution of caustic potash or iodine and finally polish with papier Joseph or with a clean pad of linen charged with a few drops of alcohol and ammonia. The plates cannot be kept clean for a long period as the action of the atmosphere very soon forms a deposit on the polished surface.

We have lately had brought under our notice a very efficient cleaning paste which is sold under the name of " Pynka," which probably consists of whiting and soapy substances which aid the chemical constituent of this paste in the cleaning of the glass.

The effect of unclean glass on collodion emulsion is much more marked than in the case of a wet collodion plate, and illustrations following page 80 show portions of an unclean plate, and also reveal pinholes, comets and other defects, due to chemical or ordinary dust having been deposited on the plate at the time of coating.

The plates are to be coated with great care as streaks and other imperfections of the surface will show when the plate is developed.

It must be borne in mind that the surface of plate glass is considerably softer than that of ordinary sheet glass, due to the removal of the hard surface in the process of polishing.

The ordinary sheet glass is therefore less liable to be injured by an excessive immersion in strong acid baths than is plate glass.

SUBSTRATA.

In most cases the writer prefers polished plates without a substratum, applying only a rubber solution to the margins to make the film hold to the glass. If for any reason, however, a substratum is desired, the following can be recommended :—

Indiarubber (best Para)	1 part.
Anhydrous benzole (or chloroform)	500 parts.

This is flowed all over the glass, and may in more concentrated form be used for edging. Albumen is a useful substratum, and the following is a good formula :—

Water	80 oz.
Albumen	1 oz.
Ammonia	1 minim.

The substratum which we have found to be most reliable is given in the following formula :—

1 —Gelatine	50 grains.
Acetic acid	3 oz.

The gelatine is warmed until dissolved.

2.—Water	½ oz.
Chrome alum	10 grains.

Take 10 parts of No. 1; 1 part of No. 2; methylated spirits, 70 parts, and filter.

The plates must be dried in a room free from dust or in a drying cupboard. Heat can be applied and the plates will be ready for use within a minute. It is, however, advisable to coat several plates, before wanted, so as to allow the acetic acid to evaporate and to cool the plate.

If the plate is not perfectly cold the ether in the collodion emulsion will evaporate during the process of coating, and an uneven film will be the result.

The presence of acetic acid also causes considerable decrease in sensitiveness, and is very marked in emulsions which are sensitized with ethyl violet.

A substratum is especially useful with emulsions which are not sensitized with the Dr. Albert's sensitizers, as several aniline dyes have a tendency to make the film float off the glass. This is prevented by the action of the picric acid which is present in Dr. Albert's sensitizers.

A substratum will also be needed if the plates are to be developed with the hydroquinone developer, which makes imperfections in the glass and polishing marks visible. If glycin is used this precaution need not be taken. A mixture of hydroquinone and glycin has been found to answer even with ordinary polished glass, but for half-tone work hydroquinone alone will give the best results and a substratum, preferably the last quoted one, will have to be used.

The Coating of the Plates.

The emulsion is well shaken in the dark-room for at least two minutes, to get the bromide of silver particles, which settle at the bottom of the bottle, after standing, uniformly and thoroughly dispersed in the emulsion. The operator should let the bottle stand for another two minutes and then coat the plate after dusting it well.

Most operators are well acquainted with the coating of the plate with collodion, but for the benefit of those who never worked collodion plates I will describe the right procedure.

Hold the plate in a horizontal position by means of a pneumatic plate-holder, dust with a soft, flat camel-hair brush, pour a small quantity of emulsion into the centre of the plate so as to form a circular pool, and gently tilt the plate first to the right hand, then to the left hand top corner, finally towards you to the left bottom corner and slowly drain back into another bottle from the remaining corner.

Do not tilt the plate too quickly and drain slowly, rocking the plate from right to left, so as to avoid thin films and streaks.

As soon as the emulsion has " set " (which can be determined when the finger makes an impression on the surface) the plate can be colour-sensitized, or, if the sensitizer has been incorporated with the emulsion, it can be placed in the dark slide for exposure.

The dark slide should be carefully dusted before the commencing of the day's work, and wiped out clean at the end of the day to free it from drainings of emulsion. Dark slides which have been used for wet collodion work should never be used for emulsion, as the dry silver nitrate forms chemical dust which causes black spots if it settles on the plate.

The emulsion must not be poured back into the same bottle, but filtered into a separate bottle. Collodion pourers have often been suggested, but I believe have not proved a success. The pouring-on bottle should not be allowed to become covered by spilt emulsion because the latter will dry and, peeling off, probably fall on to the plate during the coating. This bottle and the tin in which it is stored should be kept spotlessly clean, the mouth of the bottle to be wiped after coating. Cork or rubber stoppers should not be used, as the former cause dust spots, and the latter probably destroy the emulsion, if not made of very pure rubber. Baron Hübl suggested the following arrangement :—Take a piece of wood about 4 in. square, and cut into this a circular groove into which mercury is poured. Into this groove place a light-tight circular cardboard box open on one end. Under this box the collodion emulsion pouring bottle is placed. The bottle will be now protected from actinic light, and as the mercury forms a fairly air-tight compartment, evaporation of the solvents will be avoided. The top of the box will have to be made of (or covered with) lead, so as to make the box sink well into the mercury.

THE KEEPING QUALITIES OF EMULSION.

The collodion emulsion of commerce in its plain state before the addition of certain colour-sensitizers, especially those which are silver compounds, will keep for several years. The addition of most sensitizing dyes does not impair its keeping qualities. If, however, silver eoside or other compounds of dye stuffs with silver are added, as, for instance, the sensitizers "A," "R P," "R," "P" of Dr. E. Albert, the emulsion will only keep a few days, and in hot weather probably only a few hours.

The life of collodion emulsion thus sensitized can be greatly prolonged by keeping at a very low temperature, and if such sensitizers are to be mixed with the emulsion, it is advisable to prepare small quantities such as can be used up during the day's work. The newer sensitizers, as, for instance, Pinaverdol, Ethyl-violet and Homocol can be mixed with the emulsion and it will still keep for a very long time, showing extremely clear working qualities.

DEVELOPERS FOR COLLODION EMULSION.

GLYCIN.

Dissolve
2½ ozs. of sodium sulphite
in
4 ozs. of water distilled (hot),
and add
1 oz. of glycin
and
5 ozs. of carbonate of potassium.

The order of mixing as stated above should be carefully followed.

The solution forms a thick paste, and will keep for years, if well stoppered. For use dilute :—

1 part of glycin paste with
12 parts of water.

This forms the usual developer. If greater density is requisite, the following developer is to be recommended.

A.

Distilled water	20 ozs.
Sulphite of sodium	10 ozs.
Carbonate of potash	8 ozs.

B.

Hydroquinone	1 oz.
Water, distilled	4 ozs.

C.

Ammonium bromide	1 oz.
Distilled water	4 ozs.

Mix the three solutions and keep as stock. For use dilute 1 to 10.

This developer, introduced by Dr. E. Albert, does not keep so well, but gives extremely brilliant negatives of good density.

The density of the negatives can also be varied by increasing or decreasing the amount of hydroquinone in the developer.

Another good developer is Edinol and hydroquinone.

A.	Water distilled	200 parts
	Acetone sulphite (Bayer)	20 „
	Carbonate of potash	80 „

Add acetone sulphite *after* dissolving the potash.

B.	Hydroquinone	15 parts
	Alcohol	100 „
	Edinol	10 „
	Water distilled	100 „

Edinol is dissolved separately and added to the rest after solution.

C.	Bromide of potash	10 parts.
	Water, distilled	20 „

Take 100	parts	of solution	A.
10	„	„	B.
5—10	„	„	C.
and 1500	„	„	water

The bromide of potassium can be dispensed with entirely. The developer works very clear and gives good gradation. If greater gradation is required use more hydroquinone.

Collodion emulsion plates can be fixed with hyposulphite of sodium or cyanide of potassium. The strength of the hypo solution should be about 1 : 4.

Collodion emulsion plates must always be washed *before* development, because the alcoholic surface would repel the aqueous solution of the developer, and so cause streaks and markings.

See illustration, following page 80.

The time of development should not exceed 1½ to 2 minutes. Development can be performed whilst the plate is held in the hand or in dishes. For uniform results the dish development is preferable, especially in colour work. Accelerators or restrainers are of little use in emulsion work, where correct exposure is a desideratum. It will generally be found that the image on an accurately exposed plate appears in about 30 seconds in the hydroquinone developer, and in about 15 seconds in the glycin developer.

The above formulæ represent the developers generally in use, and in the case of half-tone work are the only developers which will give good results. For ordinary continuous tone work almost any developer may be employed—Adurol, metol, pyrocatechin, rodinal, all of which give negatives only differing in colour and brilliancy, but equally good. A higher percentage of bromide of potassium in these developers will probably be needed.

The usual hydroquinone developer furnishes exceedingly clear but hard negatives, a quality most desirable in process work, but very objectionable in the continuous tone reproduction of an oil painting, for instance. Glycin yields considerably softer negatives, especially if used in a very diluted form, but the colour of the negatives is of a yellow brown, which, however, can be changed for a more beautiful blue-grey by a short application of a very weak mercury intensifier and ammonia. This will probably serve the additional purpose of increasing the density of the negative, which is generally below the average for ordinary silver printing. The complaint often made that emulsion negatives are hard and devoid of detail in the shadows is not justified, because the softest and best graduated negatives have been made with emulsion by proper choice of developer and sensitizer.

A.—FERROTYPES.

Collodion emulsion can be used for the making of ferrotype dry plates for portraiture. The ferrotype plate is well polished with a few drops of alcoholic iodine solution, dusted and coated on a glass plate support.

To coat a ferrotype plate evenly is by no means easy. The plate should lie flat, and the surface must not show scratches or chipped-off parts in the enamel. Preservatives can be used if the plates are not immediately wanted, and those mentioned for lantern slides will well answer for the purpose. Chemically pure tissue paper should be placed between the plates when they are dry. Drying can be accelerated by means of a drying oven, or for small work a hot-water bottle or bath. To ascertain whether the plates are in good working order, one of them should be placed in the developer for about one minute without previous exposure, washed and fixed. The black enamel should not be dulled with the silver deposit, and the plates should almost look as if uncoated. Glycin and hydroquinone are suitable developers, the application of which should only last from 15 to 20 seconds. The colour of the silver deposit can be changed if different developers are used, but for most purposes the formula given will answer very well.

DEVELOPER FOR FERROTYPE PLATES.

A.

Sol. I.

Distilled water	24 ounces
Sulphite of soda (specially pure)	10 ,,
Carbonate of potash (specially pure) ..	8 ,,
Ammonium bromide	1 ounce

Sol. II.

Hydroquinone	1 ounce
Distilled water	4 ounces

Mix and label the solution A.

B.

Carbonate of potassium	6 ounces.
Sodium sulphite	12 ,,
Glycin	1 ounce
Water	20 ounces

Powder the sodium sulphite well and add the glycin after everything is dissolved.

Mix and label the solution B.

C.

Hypo	1 ounce
Water	10 ounces

For use take :—

3 drams of A
3 drams of B
9 drams of water
and 10-20 minims of solution C.

This developer gives a white silver deposit, clear shadows, and its action is rapid enough for very fast work.

The addition of colour-sensitizers, as Pinaverdol, Homocol, etc., gives very pleasing results, the coldness of the white image giving way to a warm pink shade more resembling flesh tints. The plates are also speedier and work exceedingly clear and free from fog.

A good preservative for ferrotype plates can be prepared as follows :—

Sugar candy	½ oz.
Distilled water	8 oz.

The plate is immersed in this solution as soon as the emulsion is "set," and remains in it until the repellent action of the emulsion surface is no more noticeable, then drained and dried quickly. The drying of the plate can be accelerated, but care must be taken not to overheat the plate or drying marks will result. The action of the preservative seems to be to a great extent a physical one, and is calculated to retain the permeability of the collodion surface. Decoctions of natural products, as tea, coffee, tobacco, sugar, dextrine, tannin, have been recommended for preservatives, and the properties of all are practically the same.

Amongst the best preservatives we must mention the gallic acid formula given on page 47.

Finally, we wish to point out that different preservatives greatly influence the speed of the ferrotype plates, and a suitable preservative will have to be selected according to the requirements of the operator, by making comparative tests.

B.—PHOTOGRAPHING ON WOOD.

Collodion emulsion has been found very useful in photography on wood for wood engraving purposes, giving a photographic film which is thin enough to permit subsequent tool work without chipping. The wood block is coated in the usual way with a white pigment mixed with gelatine. The edges and back of the block can be rubbed with wax to make it waterproof.

The collodion emulsion of commerce is diluted with equal parts of alcohol and ether, and the wood block coated with it in the usual way. The drying can be accelerated by placing a hot glass plate half an inch over the sensitive surface and by fanning the block. If conditions of light remain unaltered, it will be well to definitely ascertain the required exposure from a good standard negative at a given distance from the source of light, by covering the negative partly and giving a series of different exposures on the same block. The development is done in the hand and should be finished in about two minutes.

Any alkaline developer can be used, but we strongly recommend the following :—

Water	10 ounces
Metol	75 grains
Sulphite of soda	1¼ ounces
Carbonate of soda	1¾ ounces
Bromide of potassium	10 grains

Dissolve the metol in water *before* adding the sulphate. For use dilute with equal quantities of water.

Another very suitable developer is "Edinol,"* which is sold as a ready-made developer.

Glycin is not suitable, because the silver deposit is of a yellowish-grey colour and does not show the fine details in reflected light. Fix in Hypo solution 1 to 4.

A very weak solution of bichloride of mercury, and subsequent treatment in ammonia will change the brown image into a bluish-grey one and make it more visible.

It may be advisable to mix a small quantity of chemically pure glycerine with the emulsion, which will act similarly to a preservative and so ensure quicker development and more brilliant prints.

The gallic acid preservative, quoted on page 47, will also give splendid results.

It is of high importance to wet the block as little as possible, and to see that nothing remains on the surface to clog up the point of the engraver's tool or cause the wood to become friable, making the delicate lines crumble and break away.

C.—LANTERN SLIDES, OPALS AND TRANSPARENCIES.

Although the collodio-chloride emulsion gives a greater range of colour, collodio-bromide emulsion will answer most purposes, and in the case of transparencies or lantern slides which are to be made in the camera, will even become a necessity.

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* "Edinol" is a patent developer of the "Bayer Co."

The opal or glass plate is well cleaned and polished with a solution of iodine in alcohol, edged with a rubber solution or coated with a substratum (see page 37).

The substratum is well filtered, the coated plates dried in a place free from dust and coated with the emulsion. Care must be taken to shake the emulsion well before use, because the bromide of silver settles after standing for some time and almost completely separates from the ether and alcohol, when left undisturbed. The same modes of development, exposure, etc., as described for wood engraving are also to be used in this case.

If the plates are to be kept for some time before exposure, the well-known beer preservative can be used.

Pyrogallic acid	15 grains
Bitter ale	16 ounces

The plates are immersed in this solution until all greasiness disappears, then dried spontaneously. The above formula is from Sir W. Abney's "Photography with Emulsions."

Another very good preservative is made by dissolving

6 grains of gallic acid in
1 ounce of alcohol.

Of this solution,

120 minims are mixed with
10 ounces of emulsion.

A good lantern plate of higher speed can be made by adding to this emulsion

5 minims of
Pinaverdol solution, 1:500 alcohol.

This emulsion will keep well for several months.

If a transparency or lantern slide is to be made in the camera, it will not be necessary to dry the plates. They can be exposed in the moist state. If shorter exposures are desirable, the emulsion plates can be flowed with a diluted colour sensitizer, as described on page 50.

2.—COLLODION EMULSION WITH COLOUR SENSITIZERS.

A.—REPRODUCTION OF MONOCHROMES.

For this class of work it will be found best to use a collodion emulsion sensitized with Pinachrome, Homocol, Orthochrome or Pinaverdol, which dyes produce a very brilliant negative, give a good general sensitiveness, as well as colour-sensitiveness, if the latter should be required, as, for instance, in the case of coloured originals.

The emulsion is well shaken, and in dark ruby light the dye is added in the following proportion :—

1 part of Pinaverdol or Homocol solution, 1 : 500 alcohol.
40 parts of emulsion.

The sensitized emulsion will keep well, but works best after a few days. The plates must be washed before exposure.

If greater speed is requisite, immerse them in a weak silver bath :—

3 to 5 grains of nitrate of silver (recryst.) to 1000 ccm. distilled water.

The bath must be neutral, as acidity would destroy the sensitiveness imparted by the aniline dye. Neither red nor blue litmus paper should change its colour in the bath. The plate should be left in this silver bath, for about two minutes. Then expose, wash and develop. If this silver bath should cause a slight fog, use a very weak bath of glacial acetic acid before development.

The developer for monochrome continuous tone negatives should work softer than the usual hydroquinone developer, and glycin is recommended. (See page 40).

If the original is of a red or brown colour, it is advisable to use a collodion emulsion sensitized with ethyl violet.

Dissolve

1 part of ethyl purple 6B in
500 „ of alcohol.

Filter and add to every quart of emulsion 25 ccm. of above solution.

This emulsion is red-sensitive and must be handled in green light.

The plates are to be washed before exposure. Negatives made with this emulsion are soft and full of detail in the shadows. A yellow orange screen can also be used if, for instance, the object to be photographed is of a blue or violet colour.

Typewritten letters or blue prints can be successfully reproduced in this way.

B.—CONTINUOUS TONE REPRODUCTION OF COLOURED OBJECTS IN MONOCHROME.

The same course is taken as in the foregoing chapter, except in the case of a painting containing much orange and red, where a more panchromatic rendering is requisite. In conjunction with the above described emulsion a yellow screen must be used. The density of this light filter will be entirely governed by the character of the object, but for a general guidance we may point out the following conditions.

A yellow light filter should absorb the violet blue rays which the original reflects, and, by virtue of this retarding action of the filter on blue and violet in general, this permits of a longer exposure of the yellow, green and orange parts of the picture, which will be therefore reproduced in a lighter tone.

It follows that, the deeper the filter the longer will be the exposure, and the lighter the rendering of the greens, yellows and probably orange parts of the picture. A yellow filter suitable for the work can be made by bathing well-selected plate-glass coated with gelatine in an aqueous solution of either brilliant yellow or aurantia (orange), or by coating the lens itself with a collodion coloured with these dyes. Filters suitable for orthochromatic work are on the market. It is always preferable that filters be made of optically worked glass.

If a more perfect rendering of the colour values is requisite, it is advisable to sensitize the ordinary emulsion with

Ethyl violet .... 1 : 500 alcohol

of which solution 25 ccm. are added to every quart of emulsion.

This operation must be performed in a monochromatic green light. The emulsion thus sensitized keeps also indefinitely.

The plate is coated with this emulsion in green light and a solution of

"A" sensitizer.*	1 part
Spirits of wine......................	10 parts

is flowed over the plate, which is now washed and exposed.

Even without a yellow filter an excellent rendering of all pigments is obtainable.

The developer remains the same.

In place of the "A" sensitizer, Pinaverdol 1 : 500 alcoholic solution can be mixed with the emulsion in proportion 1 : 40, the ethyl violet being reduced to one-fifth of the above quantity.

The plates must be washed before exposure.

C.—TRICHROMATIC CONTINUOUS TONE NEGATIVES.

We have already given an outline dealing with the theory of trichromatic work on page 28, and can, therefore, confine ourselves to the description of the actual working methods.

A. The yellow printing or blue sensation negative.

The plate required for this negative need not show more colour sensitiveness than the ordinary wet collodion plate, and we find that collodion emulsion without the addition of any colour-sensitizer and used with a "dummy screen" gives a perfect negative for the yellow printing. The filter referred to consists of two plain pieces of optically worked glass cemented together. The object of using such a screen at all is to prevent a shifting of focus and consequent differences in the size of the three images.

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*The preparation known by the name of "A" sensitizer and sold with Dr. Albert's emulsion is an eosine silver compound, containing a small percentage of picric acid, which acts as a light filter, staining the film.

If a quicker plate is desired, we can sensitize the emulsion with eosine silver or "A" sensitizer, by pouring a solution of

"A" sensitizer......................	1 part
Spirits of wine	10 parts

over the coated plate.

As the colour-sensitiveness of a plate sensitized with eosine lies in the yellow-green and partly in the yellow, a blue-violet filter must be used, which absorbs all yellow, yellow-green and blue-green. The filter, however, passes the blue and violet. The effect of the filter is shown in Fig. I., which is a monochrome reproduction of a colour chart, published in Baron Hübl's book, "Three-colour Photography."*

Klein's light filters have been adjusted for three-colour work with collodion emulsion, and the filter to correspond with this blue-violet filter is of a pink colour, which, however, shows the same absorption as a blue violet filter but less loss of light. The latter is due to the general absorption of the blue dye.

Fig. I. shows the yellow monochrome reproduction of the colour chart.

B. The blue printing or red sensation negative.

Collodion emulsion can be rendered orange or red sensitive by the addition of cyanine, ethyl violet, chlorophyll, nigrosine and diamant black P.V.

The author introduced a cyanine silver sensitizer for collodion emulsion, but the working of all cyanine preparations is uncertain, and for general practical work the use of same has given way to easier working methods. For many purposes, however, cyanine-sensitized emulsions may be required, and with the exception of half-tone work, where brilliancy of negative is a desideratum, will certainly give very satisfactory results, if carefully handled.

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* Penrose & Co.

The formula for the sensitizer is as follows :—

A.	Chloro-cyanine	5	gramme
	Alcohol (absolute)	250	ccm.
B.	Silver nitrate	5	gr.
	Water, distilled	5	ccm.
	Alcohol (absolute)	500	ccm.
Mix	A	25	ccm.
	Alcohol (absolute)	400	„
	Glycerine	50	„
	Ammonia .880	4	„
	B	90	„

Of this sensitizer, which must be filtered and kept in the dark, add 10 ccm. for every 100 ccm. of emulsion; shaking well and using in green light only. The sensitized emulsion will only keep for 24 hours and should be kept cool.

As chloro-cyanine is not an article of commerce, it will be necessary to convert the iodide of cyanine into chloro-cyanine in the following way :—

Take a small quantity of cyanine, add concentrated pure hydrochloric acid and evaporate the brown liquid in a water bath. The dry residue is then redissolved in alcohol and a few drops of ammonia are added.

Chlorophyll has also often been used for sensitizing collodion emulsion. The sensitizer is produced by immersing ivy or other evergreen leaves into alcohol and filtering the dark-green fluid.* This sensitizer can be poured over the coated plate, which is then well washed in distilled water. It is, however, necessary to note that chlorophyll not only sensitizes for red, but also for orange, yellow and green. The sensitizer is uncertain, and we believe has never been used for practical work. It has to

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* Chlorophyll can now be obtained commercially.

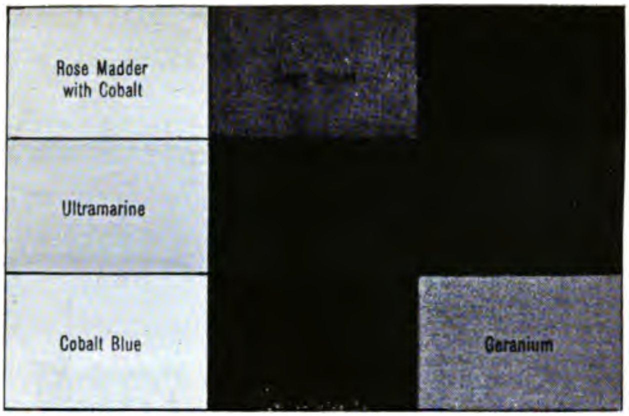

Fig. I.—Yellow Monochrome Representation of the Colour Scale.

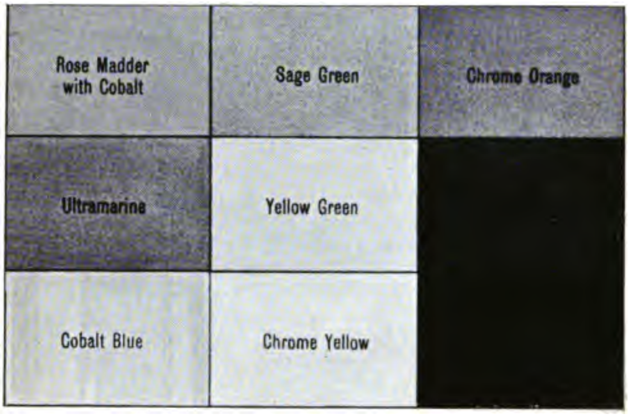

Fig. II.—Red Monochrome Representation of the Colour Scale.

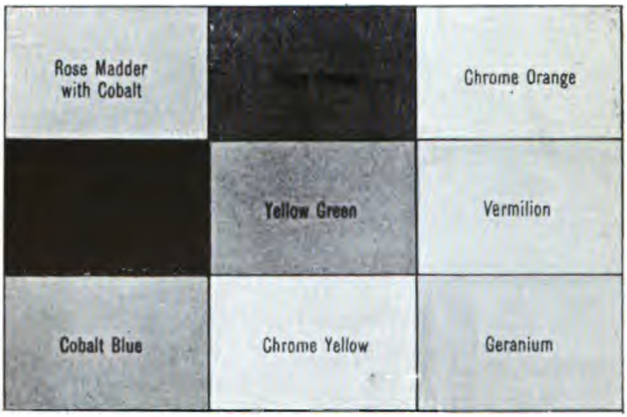

Fig. III.—Blue Monochrome Representation of the Colour Scale.

UNIV.

be used in minute quantities, scarcely staining the film, as an excess greatly decreases the speed of the plate.

Undoubtedly the best sensitizer for the blue-printing (red sensation) negative is the newly introduced ethyl violet, or sensitizer "C," which is based upon this dye.

1 gramme of ethyl violet is dissolved in 100 ccm. of absolute alcohol, and 5 ccm. of this solution are added to every quart of emulsion.

The emulsion is now to be handled in green light only, and must be washed before exposure for at least 1 minute. If increased sensitiveness is wanted, bathe the plates before exposure in a ½ per cent. silver bath.

Penrose's sensitizer "C" is in its action similar to ethyl violet, from which dye it is derived. The sensitizer "C" is added to the emulsion in proportion 1 : 40. The plate is also washed before exposure and exposed to green dark-room light only. The filter which is to be used for this emulsion is of orange red colour, absorbs all the violet, blue, green and yellow. Tolan red is very suitable for a liquid filter to be used in connection with this plate.

Fig. III. shows the blue monochrome of the colour chart.

C. The red printing or green sensation negative.

For the production of this negative, an emulsion is required which is highly green-sensitive, and emulsion sensitized with eosine and rose Bengal or with Dr. E. Albert's "A" sensitizer meets the requirements.

Eosine yellow	1 : 70 Alcohol.
Rose Bengal	1 : 70 Alcohol.

Mix and add to every quart of emulsion 25 ccm. of this dye solution. Before exposure use a silver bath

Nitrate of silver	5 gr.
Distilled water	1000 ccm.

The emulsion if mixed with the dye solution only, will keep for a long time, but if "A" sensitizer is used it will be preferable to either mix sufficient for each day's use or to coat the plate with ordinary emulsion, and after setting of the emulsion flow the following solution several times over the coated plate :

" A " sensitizer	1 part
Spirits of wine	10 parts

and expose at once.

The filter to be used for this negative, if " A " sensitizer is used, is of a yellow colour. Picric acid will answer well in a liquid filter. The absorption of the filter must include all the violet and blue rays. We need not absorb the red, because the emulsion used is quite insensitive for the red and orange. If however, eosine, rose Bengal and silver bath are used, the filter must be of a green colour, showing a wider absorption band.

A colour scale should be used for the practical tests in standardizing collodion emulsion light filters, and the corresponding colour-sensitizers for collodion emulsion in three-colour work. A grey scale, made of different shades of exposed platinotype paper, should be rendered in equal densities in all three negatives, and the colour scale should be rendered as shown by the three monochrome prints without regard to the appearance of the negatives.

Dr. Eder found that an addition of about 2 ccm. of a 1 : 500 solution of monobromofluorescinate of sodium to every 10 oz. of an emulsion sensitized with ethyl violet greatly increases the speed, but also confers a slight green-sensitiveness on the emulsion, which must be corrected by means of a filter. Tolan red will be found to give the required absorption for such plates. In the case of a slight fog, a very weak acetic acid bath should be used before development. It is not advisable to use acids before exposure, for obvious reasons.

All references as to the production of the filters which are to be used with collodion emulsion are only to be taken in an indicative sense. The making and adjustment of such filters is fully described in Baron Hübl's " Three-colour Photography," and cannot be dealt with in the limits of this little handbook.

The developers will have to be selected according to the requirements of the printing process. Collotype requires a different character in the negatives to that for bichromatized celluloid films, but for most printing processes the hydroquinone developer given on page 40 will give a good range of densities, and will answer very well.

It may be useful to recapitulate that glycin gives softer negatives than hydroquinone, and that the density of the silver deposit can be regulated by an increase or decrease of the developing compound. Further, that plates washed before exposure produce softer negatives than unwashed ones, that the addition of bromide of potassium in the developer increases its clear working qualities. If the negatives require intensification, the following intensifier will be used.

Water	30 ozs.
Common salt	60 grains.
Bichloride of mercury	60 „
Hydrochloric acid	5 minims.

The plate is well washed and drained after the fixing, and bleached in this solution. Then well washed again and flowed with

Liquor ammonia	3 drams.
Water	4 oz.

The negative takes a blue-grey tint, and is of excellent printing quality. The negative is well washed again, dried and varnished with spirit varnish.

The film is now sufficiently protected to allow for the retouching, which will chiefly be confined to the strengthening of high-lights.

D.—PROCESS WORK.

(a) Line Reproduction.

The very pronounced tendency to spread, due to a scattering of light in the film, and to reflection from the glass, have made collodion emulsion unsuitable for very fine line-work.

Ordinary line-work, however, can be done with collodion emulsion, preferably with unsensitized emulsion.

Various working methods have been suggested to overcome this difficulty and some have proved to be of real practical value. The image of a collodion emulsion negative is not formed on the film as in the case of the wet collodion process, but in the film. The film itself containing bromide of silver furnishes the picture-forming metallic silver, which the oxidizing agent (the developer) has reduced from the silver sub-bromide in the film. The developer does not act in a physical but in a chemical way. Backing of the plates and slight under-exposure, addition of yellow staining substances to the emulsion, as for instance, picrate of ammonia, thiazol yellow, canary yellow, have proved effective. It is desirable to back the plates and we can recommend the following method :—

Make up the following solution :—

Glycerine...........................	1 part
Alcohol	2 „
Water	2 „

In this solution soak black paper which is used for wrapping up dry plates until pliable, and squeegee on to the back of the plates before coating.

This will form a very efficient backing and will greatly reduce halation.

The usual methods of guarding against vibration, stopping down of the lens, etc., should be familiar to the reader and need not be mentioned.

It is advisable to coat the plates with one of the substrata mentioned on page 37, not to over-expose, and to develop with hydroquinone (page 40).

The negative is intensified with :—

Bromide of potassium	2 ounces
Sulphate of copper	1½ „
Water	68 „
Nitric acid, pure	35 minims

When the plate has been fixed and well washed, sufficient of the above solution is poured over and allowed to remain on until the image is bleached.

Rinse for a few seconds. Prolonged washing will injure the density.

Flow the plate with sufficient of the following solution to darken the image :—

Nitrate of silver..................	1½ ounces
Water, distilled	100 „

Rinse well and varnish.

(*b*) Half-Tone Work.

Collodion emulsion has been chiefly applied to half-tone work, because of its isochromatic qualities, which permit the reproduction of the more difficult subjects, as for instance, blue prints, yellow or red lettering on black ground, etc., where the wet collodion plate process is useless. The character of the half-tone dot of a collodion emulsion plate, after intensification and reduction is very much like that of the wet plate.

A spreading of light in the film necessitates closer screen distance and smaller stops, and more "flashing" or exposure on white paper will be found imperative.

Baron Hübl in his book on collodion emulsion, says :—

"In addition to a suitable opacity of the high-lights and clearness of the deepest shadows, we require in a good negative a correct rendering of the middle tones. This condition is by no means easy to fulfil, because it lies in the nature of the photographic process, that the amount of reduced bromide of silver is not proportional to the intensity of the light, which caused its reduction during an exposure. Every photographic film requires a certain length of exposure to produce a visible reduction, and the duration of such an exposure will be governed by the intensity of light, so that quite a disproportionate increase of exposure will be rendered necessary by any reduction of its intensity.

"To start the chemical decomposition in a photographic film, a certain length of exposure will be required, which is determined by the light sensitiveness of the film and the intensity of the light.

"As soon as the decomposition is started, we may assume that the remaining reduction of the bromide silver particles progresses proportionately with the time.

"Rays reflected from the white parts of the original will immediately start this transformation in the photographic film, whereas those reflected from darker parts will begin to act later. If we now develop after a certain length of exposure, we shall notice that the white parts of the picture are quite disproportionately dense, when compared with the middle tones.

"Every photographic process has a tendency to increase the depth of the shadows.

"It is a well-known fact that the portrait photographer has to lighten the shadow parts of his model by means of reflectors so much, that to our eye the shadows appear far too light, yet the negative will show deep shadows."

And again : " With a certain low intensity, the light loses its property of decomposing bromide of silver. Exactly as a certain temperature is requisite to cause solution of a body, so is minimum of light intensity requisite to cause a reduction which can be made visible by means of development."

As explained previously, collodion emulsion requires smaller working apertures than a wet plate, the intensity of light is therefore greatly diminished, and to produce an initial decomposition of the sensitive compound, a considerably longer exposure on white paper will have to be given, or the shadow dots will never show that nucleus which forms the foundation of the strong, yet very minute shadow dot, and this can only be secured by repeated attacks of reducing chemicals to which the dot must offer sufficient resistance.

A writer in one of the technical journals, for example, proposes working apertures of *f*/96 for the picture and *f*/192 for the white paper, giving practically one half of the exposure on white paper whenever collodion emulsion is used for the direct half-tone colour process.

Of course, such extensive white paper exposure is only justified by the low intensity of light due to colour filters* and very small lens openings. Collodion emulsion in its raw state, *e.g.*, before the addition of colour-sensitizers, permits, however, the use of considerably larger apertures. The effect of the different colour-sensitizers on the formation of a half-tone dot, is a rather mysterious one, and still invites investigation.

We find that collodion emulsion before the addition of an aniline dye, gives very sharp half-tone dots, and this, even with comparatively large apertures, but after aniline dyes have been added to the emulsion, the dots become more or less unsharp and indistinct, the degree of unsharpness differing with the different dyes, and being greatly increased by the washing of the plate before exposure. Various theories have been propounded to explain the latter effect, but we believe it is only due to an evaporation of the water during the somewhat long exposure, which excites vibrations of the atmosphere in immediate vicinity of the image and causes a blurring of the minute dots. This theory, we believe, is confirmed by the facts that an unwashed plate presenting an alcoholic surface gives sharper dots than a washed one, that a collodion emulsion made with solvents containing a high percentage of water shows also the same defect, and finally that plates which are exposed in cold rooms are freer from it than plates exposed at high temperatures.

Halation is also partly responsible for this defect, and picric acid and other yellow dyes, *e.g.*, tartrazine, have been successfully introduced into the emulsion to prevent halation.

In cases where such a course cannot be adopted, we recommend backing the plates with ordinary black paper, which has been soaked in a bath containing glycerine, spirit and water. See page 56. The glycerine will make the paper very pliable, and such paper pressed on to the back of the plates, and removed again before development, will generally greatly decrease halation.

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* It has been suggested that the colour filter may be withdrawn during the exposure on white paper to reduce the time.

Dr. Albert prepared an eoside of silver compound, named sensitizer "A," which will not only increase the speed of the emulsion and give it isochromatic properties, but will also secure sharp dots with clear glass in between, and when intensified and reduced, yield negatives which in no way differ from those made on a wet plate.

The developer most suitable is the hydroquinone formula, page 40, or the glycin formula, page 40, or both mixed in equal proportions. Hydroquinone gives ideal half-tone negatives, but requires exceedingly clean glass, free from scratches or other defects, which glycin never makes visible. To combine the good qualities of both, we have proposed a combination of the two, and found it to work remarkably well.

The time of development is of importance. One to one and a half minutes should be the maximum, no accelerator nor restrainer should be used, and all operations should be standardized. The plate should never be exposed to an excess of the dark-room light, however safe the latter may be.

For black and white subjects, ordinary emulsion may be used, but if the original is coloured or if a faster plate is requisite, the emulsion should be colour-sensitized.

The plate is coated in the usual way, page 38, and "A" sensitizer diluted in the proportion of 1 to 10 with spirits of wine, is poured four times over the coated plate. The plate is then exposed. Round or square stops or both may be used.

The tendency of the high-lights to close up, will rarely necessitate the use of cut-out corner stops, and will always compel the operator to work with a very small screen distance.

If large plates are to be exposed, special provision will have to be made to keep the Emulsion cool, because they necessitate the colour-sensitizing of the emulsion by mixing the sensitizer with it in proportion of 1 to 10, and such sensitized emulsions must be kept below 45° Fahr.

PREPARING THE EMULSION.

The operations must be performed in a ruby light only in the case of "Sensitizer A," and in green light for "Sensitizer C."

The sensitizer "A" is best added only to a sufficient quantity of emulsion for daily use. Though not impossible to use the sensitized emulsion a day or two old, there is a risk of foggy negatives by doing so, especially in hot weather. The plain emulsion will keep indefinitely, but the colour-sensitized emulsion deteriorates from day to day.

The sensitizer must be kept in the dark, and not shaken, the clear portion being decanted off for addition to the emulsion.

The emulsion must be thoroughly well shaken in a partially filled bottle for about three minutes. The object of this is to redissolve any precipitate of bromide of silver which settles at the bottom of the bottle after standing for any length of time.

It is very essential that the sensitized emulsion be kept in a cool place, and in hot weather it should be cooled with ice, especially before sensitizing. The emulsion works best when kept below 60° Fahr. A higher temperature tends to fogging.

Take 1 part of the filtered sensitizer "A" for mixing with 10 parts of emulsion. The sensitizer is added gradually in small portions, shaking the bottle vigorously between each addition.

The emulsion, after being allowed to stand for two minutes, is now ready for use.

The plates are washed after the exposure, to free the film from the alcohol and ether which would repel the aqueous developer, and so cause streaks and markings. See illustration, following page 80. The plates are developed in dishes for one to one and a half minutes in the summer, and two minutes in the winter. They are fixed and intensified, reduced, etc., as described on page 56. Lead intensifier is very suitable for building up a very faint shadow dot, the Farmer reducer of hypo and ferricyanide of potassium being used before intensification.

REDUCER.

(To be used before intensification with lead).

(A)	Ferricyanide of potassium	1 ounce
	Water	25 ounces
(B)	Hypo	1 ounce
	Water	10 ounces

For use mix

(A)	1 ounce
(B)	2 ounces
Water	10 „

INTENSIFIER.

Water (distilled)	25 ounces
Ferricyanide of potassium	1 ounce
Nitrate of lead	1 „

Dissolve and filter.

The reduced and washed negative is left in the intensifier until yellow right through, washed, rinsed with

Hydrochloric acid	½ ounce
Water	100 ounces

rinsed again under the tap and blackened with 3 per cent. solution of sodium sulphide, rinsed again under the tap, cleared with the hydrochloric acid solution, rinsed again under the tap, gummed and dried.

If the high-lights are fully exposed, copper and silver for intensification, page 56, and cyanide and iodine for reduction will be found most suitable.

IODINE REDUCER.

Iodine	40 grains.
Potassium iodide	80 „
Water	20 ozs.

Bleach the negative with this solution, rinse under the tap and apply a weak solution of cyanide of potassium until the shadow dots are of the required size. Wash and blacken with a solution of sodium sulphide. Wash and varnish with

Gum arabic	4 oz.
Water	40 oz.
Carbolic acid..............	35 minims.

The plates may be dried by heat and may also be stripped by first coating the film with rubber solution. and then with stripping collodion, or a gelatine coating can be given instead of rubber and collodion.

The new dyes, Pinaverdol and Homocol, may be used for half-tone work, but as the plates must be washed before exposure, the same sharpness of dots cannot be obtained. The emulsions sensitized with the above dyes are not very fast, but are extremely clean working. The dyes are dissolved in alcohol in proportion of 1 to 500, and about 40 ccm. of the dye solution is mixed with the raw emulsion.

As Homocol and Pinaverdol sensitized emulsions are not only green-sensitive, but slightly orange-sensitive, very faint ruby light is to be used in the dark-room. A very safe dark-room light for such emulsions is prepared by staining gelatine-coated glass plates with

1. Aurantia,
2. Eosine,
3. Methyl violet,

and binding all three together. Such safe lights pass the extreme red of the spectrum only.

Physical intensification of collodion emulsion negatives has many advocates, but we have never found it necessary to resort to it. It may be interesting, however, to quote Baron Hübl, who in his work on collodion emulsion, says :—"Collodion emulsion plates can be intensified by physical methods, and whenever possible such methods should be made use of. The chemical intensifier increases the density of the whole negative, but physical intensification deposits considerably more silver in the high-lights, increases the brilliancy of the negative without injuring the fine details. For physical intensification, mixtures of silver nitrate with reducing substances, such as metol, hydroquinone, and pyro are used, and the addition of an acid (acetic, citric, sulphuric) retard the reduction, so as to conveniently control its effect. If a negative is flowed with such a solution, metallic silver in a fine state of division is deposited on to the silver particles of the picture.

The best results in collodion emulsion are obtained with the following metol intensifier :—

A.	Metol	3½ drachms.
	Citric acid	2½ „
	Water, dist.	40 ozs.
B.	Silver nitrate	½ oz.
	Water, dist.	50 ozs.

The negative is well rinsed after the fixing, to remove every trace of hypo. A small quantity of " A " solution is poured over the plate to remove the traces of water. One volume of " A " solution is then mixed with $\frac{1}{10}$ volume of " B" solution, and the negative intensified in the usual way. It is remarkable that negatives take intensification better if they have been dried after fixing and washing than if intensified before drying."

(*c*) Work with the Metzograph Screen.

As Wheeler's Metzograph Screen is frequently used, more especially in four-colour work, the methods of working when emulsion is employed will somewhat differ from those of the wet collodion process. In the first instance it is well to consider the nature of the screen. Pyro-betulin is precipitated on a glass plate as a reticulated acid resist. The glass is etched with hydrofluoric acid and a corresponding reticulation of the surface will be the result. The resist having been removed, the screen presents a clear glass appearance, slightly dulled by the means of glass reticulations which act like lenses in bringing the rays

Plate VI.

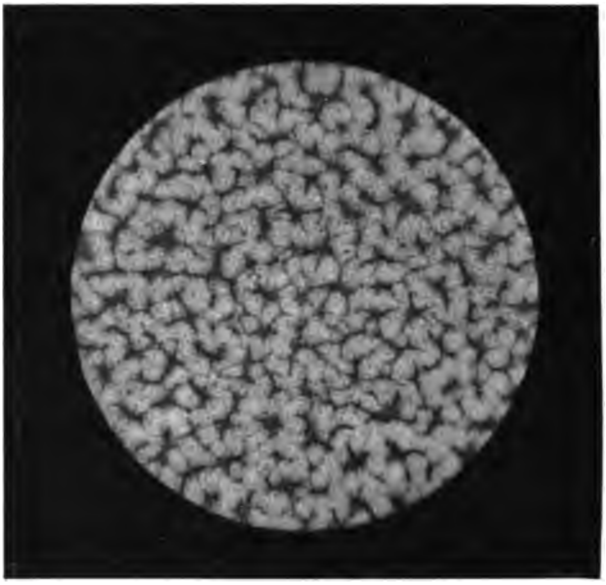

Fig. I.—Metzograph Negative enlarged 40 diameters, showing the effect of correct screen distance.

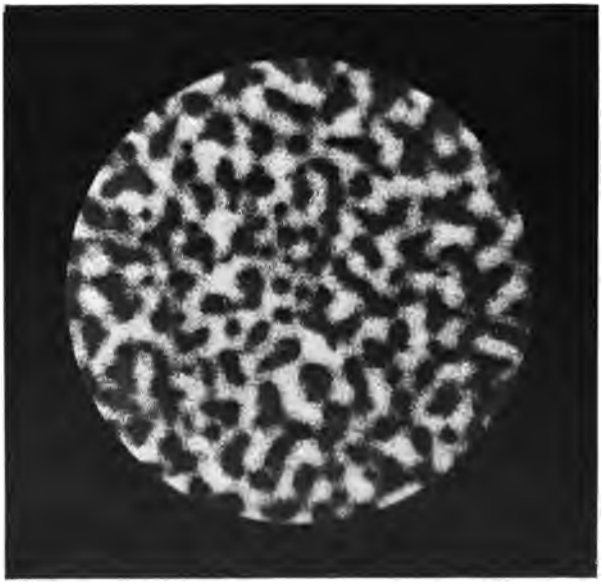

Fig. II.—Incorrect screen distance with Metzograph Screen.

Photo-Micrographs by Mr. Edg. Senior.

NIV

of light to a focus. These lenses or reticulations are extremely minute, and there is practically no latitude in their focus. Now this forms the most important feature in metzograph work, because of its bearing on the correct screen distance. In most cases the usual screen holders do not come close up enough to the plate, and the focus of the reticulations become a little disc of diffusion, joining up with the next disc, and when intensified clog up the high-lights without giving a shadow grain at all. This effect is very marked in collodion emulsion metzograph work, and the utmost precision and care is requisite to get good results. The only proper way of ascertaining this fixed screen distance—for the distance will, if the same stop is used, be always the same—is to paste pieces of paper on the corners of the screen so as to rest the plate on it, and gradually build up by adding paper until the sandy appearance of the negative gives way to a beautiful reticulation consisting of very fine hairy-looking branches of good intensity and free from halo, *vide* Fig. I., facing page 64.

The illustrations show distinctly the difference between the correct and incorrect screen distances. Both negatives were taken with the same stop, same flash, same exposure, the only difference being in the screen distance, which, if incorrect, sacrifices detail, produces coarse grain and makes the work of printing on metal extremely difficult.

Another very important point we have to mention is the question of lens aperture. As there is no light obstructing pigment on the metzograph screen very small stops are practical and necessary, *f*/64 being the largest stop that may be used. F/192—*f*/384 are the working aperture stops which have given us the best results in collodion emulsion work. The flash on white paper cannot be dispensed with, and if the copy is dark will, with a stop of half the diameter of the exposure stop, amount to one-half of the total exposures. Once these two points—screen distance and stop—have been determined the work becomes perfectly mechanical, and is considerably simpler than the making of an ordinary half-tone negative.

For many subjects, as pencil drawings, pastels, and fourth printing plates in three-colour work the metzograph screen will beat the ordinary half-tone in range of gradation, in three-colour work, in better colour rendering and less loss of colour, because the breaking up of the image is not based upon the more or less mechanical devices of the cross-line screen, but upon the physical properties of the reticulated glass, which does not exhibit the often disagreeable shortcomings of the photo-mechanical rendering of gradation, being more of a photographic nature. If exposure will permit, ordinary emulsion can be used, and the methods of developing, intensifying, etc., of the ordinary screen negative are also employed here. Although not pertinent to the subject it may be of use to mention that the printing on metal and subsequent developing of metzograph negatives requires great care as the high-lights have a tendency to break.

(*d*) Direct Three-Colour Half-Tone.

Although dry plates have been and are on various occasions employed for the making of direct colour and screen negatives, there is no doubt that collodion emulsion is most admirably suited for the purpose, and this for reasons, which cannot fail to impress by their importance.

Baron Hübl says :—" Collodion emulsion gives broad sensitizing bands which are in no way affected by screening defects, and which are so very desirable for our purpose." And again : " The screening defect is more noticeable with gelatine plates, than with collodion emulsions, because gelatine quickly absorbs dye solutions and can be deeply stained by weak solutions. It follows that the curves of sensitiveness of a colour-sensitized dry plate show rarely, if ever, any conformity with the actual colour sensitizing of the dye."

If the less refrangible rays are to act on our plate, collodion emulsion may also be superior to dry plates in point of exposure. Further, the working with collodion emulsion is simpler and more convenient, especially in the case of large sizes. Plates up to any size can be made immediately, and all operations of washing, developing, etc., can be performed without dishes.

Further the half-tone dot on a collodion emulsion plate is sharper and much better defined than on a dry plate, exposures are considerably shorter and the after operations require less time, especially the drying, which can be done by heat.

We believe that the first in this country to make commercial use of collodion emulsion for trichromatic screen work was the firm of Carl Hentschel. Their process, however, has been a secret one, and, so far as the making of the emulsion is concerned, is still a trade secret.

In 1901, the author, being in charge of the experimental department of Messrs. Penrose & Co., worked out a satisfactory direct three-colour process with collodion emulsion, which Mr. E. S. Padmore, who greatly assisted him, introduced to the well-known firm of Messrs. Swain and Son, in Barnet. A similar process was published in the German edition of *Process Work*, No. 17, June, 1901, about two months before the Imperial High School of Graphic Arts in Vienna published a direct three-colour process.

Messrs. Howard Farmer and Guy Symmons, at the Polytechnic School of Photography, who worked a direct three-colour dry-plate process at the time, were the first to teach the process in this country, and to make valuable additions to it, whilst conducting a series of experiments, with the object of solving the problems of irradiation, which is so marked in collodion emulsion negatives made with very fine screens. *Vide* Plate IX., following page 81.

Scientific research, aided by practical experience, led to rapid progress being made in direct three-colour half-tone work with collodion emulsion during the last three years. Prof. Dr. J. M. Eder published valuable spectral analytic studies having direct bearing on the subject; Prof. Dr. Valenta introduced the excellent red sensitizer, ethyl purple, and Baron von Hübl the dye Pinaverdol. Light filters have been standardized, curves of sensitiveness and absorption bands have been accurately measured, and their relations toward each other have been the subject of much experimental work.

The various technical schools teach the process in the evening classes, and every opportunity is afforded for making rapid progress in collodion emulsion three-colour work.

WORKING INSTRUCTIONS.

There are four different methods of making the colour and screen negatives with collodion emulsion.

(1) To use collodion emulsion which has been made colour-sensitive by the addition of pure aniline dyes. Such emulsions will keep well, work extremely clean and perfectly free from the well-known "spot and comet" troubles of the other method, but the plates must be washed before exposure, and therefore cannot give the same sharp half-tone dot as unwashed plates. They are also too slow for dark subjects, even if the illumination is a very good one. The dyes which are of great value are acridine for the yellow printer, eosine or erythrosine for the red printer, and ethyl violet for the blue printer.

The absorptions of the filters should be adjusted so as to suit the sensitiveness of the respective emulsions.

In the place of acridine-sensitized emulsion, ordinary collodion emulsion, without the addition of sensitizers may be used for the production of the yellow printing negative, the filter to be a blank filter, consisting of two pieces of optically worked glass sealed together or a tank filled with water.

(2) Emulsions exactly as above, but plates immersed before exposure in a ¼% to ½% nitrate of silver bath. Nitrate of silver is known to be the best chemical sensitizer, and forms with the aniline dyes silver compounds, which greatly increase the speed of the plates. This method of working has many advocates and is practised in several

large establishments with great success. The quality of the nitrate of silver and the distilled water will have to be carefully considered.

Great cleanliness is a *sine qua non*, and unless everything necessary is attended to with the most unsparing exactitude, this method of working is one of the most trying we have experienced. On the other hand, it yields extremely fast plates and good colour sensitiveness. The silver bath must not be acid and the very best re-crystallized nitrate of silver should be used. The filters have to be accordingly altered.

(3) Collodion emulsion sensitized with a so-called panchromatic sensitizer, Homocol, Pinaverdol, or Pinaverdol and Ethyl violet combined.

Pinaverdol and Ethyl violet, a combination first proposed by Baron Hübl, gives very clean emulsions of good keeping qualities, and is fairly panchromatic. The filters should be considerably deeper in colour, and the possibility of getting direct three-colour half-tone negatives of anything but very light water-colours is very doubtful. This method of work is admirably suited for the indirect three-colour work.

(4) Collodion emulsion used in its unsensitized state for the yellow printer, sensitized with "A" sensitizer for the red printer and with "C" sensitizer for the blue printer. This is the most usual method of working, although greater care must be taken than in No. 1 and No. 3. Wet collodion must not be worked in the same dark-room or the same dark slide. Greater care must be taken over the cleansing of the plates, which extra labour, however, is well repaid by a beautifully defined half-tone dot, great sensitiveness, and good colour rendering. The filters can also be considerably lighter, because the sensitiveness of the emulsion is well defined and the filters are merely correction filters.

Having stated the *pros* and *cons* of the four different methods which may be selected, we give simple instructions.

Method I.

Emulsion for the Yellow Printer.

Dissolve 1 part of Acridine N.O.* in 300 parts of absolute Alcohol, filter through paper and add to

1 quart of collodion emulsion
20 ccm. of Acridine solution.

If the exposure is long, bathe the plate in a borax bath,

1 part of cold saturated borax solution
3 parts of water, distilled.

Baron Hübl says in "Three-colour Photography,"† "The intensity of the filter must be regulated by the green sensitiveness of the plate. If green pigments are rendered too light, the filter must be made deeper in colour."

Emulsion for the Red Printer.

Dissolve 1 part of Eosine yellow,
3 parts of Uranine
in 300 parts of alcohol;

filter and add to

1 quart of emulsion,
30 ccm. of the above dye solution.

The light filter to be used will be Naphthol yellow or picric acid.

Emulsion for the Blue Printing Plate.

Dissolve 1 part of Ethyl purple 6 B.
in 500 parts of alcohol;

filter and add to

1 quart of emulsion
25 ccm. of dye solution.

The Emulsion should be handled in green light and washed before exposure.

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*Messrs. Leonhard, Mühlhausen-am-Rhein.
†Penrose & Co., London.

LIGHT FILTERS FOR METHOD I.

Use 5 mm. tanks with following solutions :—

Yellow Printing.	Methyl violet, 1 : 10.000.
Red Printing.	Picric acid 1 : 10.000.
Blue Printing.	Aurantia 1 : 1000.

Method II.

Emulsions sensitized as in Method I., but bathed for two minutes in

Nitrate of silver (re-crystallized) neutral	¼ to ½ oz.
Water, distilled	100 oz.

Filter bath before use and test with red and blue litmus paper. The silver-bath must not show acid reaction. Filter solutions to be used as above, but more concentrated, *vide* Hübl "Three-colour Photography."

Method III.

Dissolve in water-bath

1 part of Pinaverdol*
in 500 parts of alcohol, absolute.

Filter and add to

1 quart of emulsion,
40 ccm. of Pinaverdol solution, and
10 ccm. of Ethyl violet solution 1 : 500.

Use in the dark-room very deep red safe light, passing the extreme red of the spectrum only. Wash plates before exposure.

Use tanks with 5 mm. separation.

Yellow Printer.	Höchster New Blue,	1 : 5000.	
Red Printer.	Acid green	1 : 100	10 parts.
	Auramine	1 : 100	150 parts.
Blue Printer.	Biebrich Scarlet	1 : 1000	
	Aurantia	1 : 500	

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*Messrs. Fuerst Bros.

Method IV.

The yellow printing plate can be made with plain collodion emulsion and a "dummy" filter (no coloured films sealed between the glasses) or the collodion emulsion may be colour-sensitized with Canary II.* in which case a light filter will have to be used. This latter method has been suggested by Mr. A. J. Newton, of the L.C.C. School of Photo-Engraving.

Collodion emulsion sensitized with this yellow dye works very clean, and if the plates are washed before exposure, is also faster than ordinary collodion emulsion. The proportion which we have found most suitable is :—

Canary II. (hot concentrated solution)	1 part.
Collodion emulsion	50 parts.

We believe this emulsion to be of good keeping qualities, although our experience with it is not extensive at the time of writing. Larger stops can be used with this sensitizer than for collodion emulsion sensitized with other dyes, which is probably due to the intense yellow colouration of the film preventing halation.

The Red Printing negative is made with collodion emulsion sensitized with Dr. Albert's "A" sensitizer, which, as already stated, is composed of eoside of silver, picrate of ammonia and glycerine. The first substance sensitizes emulsions for yellow green, besides increasing the general sensitiveness; the second prevents halation and the third keeps the emulsion from drying too quickly during long exposures.

There are two different ways of introducing this sensitizer into the emulsion, *e.g.*, to mix one part of the sensitizer with 10 parts of emulsion, or to dilute the sensitizer, and pour it over the coated plate. For a beginner we should recommend the second method as being the more reliable one, although the first method presents many features which the experienced operator does not wish to dispense with, for instance, uniformity of sensitiveness all over the plate, comparative freedom from dust-spots, greater speed and convenience. This emulsion, however, is most liable to fog, especially if worked at temperatures over 45° Far. In hot weather or in dark-rooms adjoining over-heated studios, the emulsion would require cooling with ice, especially at the time of mixing the sensitizer with the emulsion. Ten parts of emulsion having been well cooled, are mixed with one part of the sensitizer "A," which has been filtered previously; only small quantities are mixed, sufficient for each day's use. The sensitizer must not be poured into the emulsion at once, but is to be introduced in very small quantities and the emulsion is to be shaken vigorously.

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* **Read, Holliday & Sons, Ltd., Huddersfield.**

Emulsion sensitized in this way will generally work for a few days, provided it is kept in a refrigerator or an ice box. It will, however, increase in speed very considerably. The plates are washed after exposure and deep red light is to be used in the dark-room. Time of development is not to exceed two minutes and direct dark-room light, which is only comparatively safe, should not strike the plate. If the dark-room lamp is turned towards the wall, on which a sheet of white paper has been fastened, a very safe and even illumination is diffused all over the room.

If the operator, however, is not familiar with collodion emulsion, he will dilute one part of sensitizer "A" with 10 parts of spirits of wine (probably certain kinds of methylated spirit will do); this being filtered and flowed four times over the coated plate will sensitize same effectively. The drainings can be re-filtered and used again. When the solution is exhausted, surface fog will result. It has been found advisable not to use the diluted sensitizer more than twice.

The colour filter used absorbs the violet and blue rays.

The Blue Printing negative is made with collodion emulsion sensitized with sensitizer "C," in proportion 1 : 40. This sensitizer, consisting of ethyl violet which has undergone chemical treatment, and to which other dyes have been added to check halation and increase speed, has been introduced by the author and is now an article of commerce.

The sensitized emulsion will keep well, works very clean and gives a half-tone dot of good opacity, though showing a tendency to be "woolly."

The difficulty has to a great extent been overcome by the introduction of the yellow flame carbons used in the enclosed arc lamps, which shorten the exposure and so permit smaller stops being used. The type of enclosed arc lamp selected should be one burning the flame carbons in a current of high voltage, thereby giving a long arc, and the exposures will be reduced to about one-fourth of the ordinary.

3.—THE MAKING OF COLLODION EMULSION.

We may divide collodion emulsion into two classes; one for use in its colour-insensitive state, the other for orthochromatic work, suitable for colour-sensitizing with aniline dyes or aniline silver compounds.

We will begin with the former. Sir W. Abney in his work, "Photography with Emulsions," says:—"If a preservative be used as a sensitizer, there can be no doubt that a collodion should be used which is as porous as possible, to enable it to surround the particles of the sensitive salt."

This clearly explains the action of a preservative in a collodion dry plate, which plays an important part in its production. "This porosity has another advantage, which is, that when the preservative is washed off previous to development, the sensitive salt is immediately accessible to the action of the developer."

We insert this quotation as a preliminary to the formulæ which will be given without further comment, as a full explanation of the action of preservatives would form sufficient matter for another volume. Those who require more elaborate details concerning the scientific part of the subject, such as is quite necessary for a full understanding of the difficult task of making collodion emulsion, cannot do better than study Sir W. Abney's "Photography with Emulsions" and Baron von Hübl's "Collodion Emulsion."

H. Cooper's Collodion Bromide Dry Plates.*

Prepare a stock solution of plain collodion by dissolving 160 grains of pyroxyline in 6 oz. of abs. alcohol and 10 oz. of ether. Also make an alcoholic solution of zinc bromide, 80 grains to the ounce. Even after filtering this solution will throw down a deposit upon keeping and this must be carefully left undisturbed. To make 10 oz. of washed emulsion, take 5 oz. of the above collodion and add to it 1 oz. of the zinc bromide solution and 20 minims of the syrupy lactate of ammonia. Sensitize with 150 grains of silver nitrate, dissolved first in 80 minims of water and then in 3 oz. of strong alcohol. Boil together and add it to the bromised collodion at once. Wrap the bottle in a thick cloth to retain the heat as long as possible. It is well to add the lactate immediately before the silver.

The emulsion is ripe in about twenty-four hours, but it is an improvement to keep it for a longer time, up to three days. At the expiration of the ripening period, twenty minims of the strongest nitric acid are to be added and the emulsion well shaken. It is well to add the acid just before the washing instead of at first. The emulsion is precipitated by mixing it with twice its bulk of the following organifier, and when the pellicle has fully separated and set, washing for some time in water, containing a little nitric acid (½ oz. to 1 gallon) and finally in several changes of pure water. The mixture—

Tannin	500 grains
Gallic acid......................	200 „
Grape sugar	200 „
Strong acetic acid	10 oz.

or a proportionately less quantity of acetic acid, to be dissolved in water and make up to 100 oz.

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*Sir W. Abney's "Photography with Emulsions."

When dry, dissolve the above quantity of pellicle in 5 oz. absolute alcohol and 5 oz. of extra purified ether ·720, filter.

Dr. Dawson's Collodion Emulsion.

This is a collodion emulsion process to which an organifier has been added in the following :—

COLLODION.

Pyroxyline	8 grains.
Cadmium bromide	7 „
Ammonium bromide	2 „
Ether ·725	½ oz.
Alcohol ·810	½ oz.

The collodion should be allowed a few days to settle and is then decanted.

To sensitize, the following mixture is made up :—

Silver nitrate	13 grains.
Acetic acid	2 drops.
Glycerine	1 drachm.
Alcohol ·830	4 „

This is added to the collodion to form the emulsion and after standing for about one day, two drops of hydrochloric acid are added. It is again allowed to rest for 24 hours.

Now the emulsion is poured into a flat dish to allow the ether and alcohol to evaporate, which will be in 4 to 6 hours. The pellicle is now covered with water for one hour and after pouring off is covered for the same length of time with :—

Tannin	5 grains.
Gallic acid	2 „
Acetic acid	2 drachms.
Distilled water	1 oz.

The pellicle is then washed until all traces of acid are removed, the water pressed out and the pellicle dried by spreading on blotting paper.

The pellicle must not be dried with alcohol, which would dissolve the gallic acid and the tannin.

To re-dissolve the pellicle, use equal quantities of ether and alcohol. The pellicle should be soaked in alcohol for 12 hours before adding the ether.

Collodion Emulsion (Unwashed).

This emulsion is described in Woodbury's "Encyclopædia of Photography."

In this process the emulsion is not washed until after the plates are coated. The collodion is prepared in the following way :—

Ether ·720	7 oz.
Alcohol ·820	4 oz.
Pyroxyline (high temperature)	70 grains.
Zinc bromide	120 ,,

The ingredients are mixed in the order given and allowed to stand for 24 hours.

180 grains of nitrate of silver are now dissolved in a test tube with 90 minims of boiling distilled water. In another test tube 1½ oz. of alcohol are boiled and when both solutions are at their boiling point, add one ounce of the alcohol to the silver solution. The test tube containing the silver solution, the tube containing the remaining ½ ounce of alcohol and the bromised collodion are next all removed to the dark-room—a room lighted only by yellow light. The silver solution is then added drop by drop to the collodion, which is kept violently agitated with a glass stirring rod. When all the silver solution has been added, the remaining half-ounce of alcohol is poured into the tube to dissolve the crystallized silver, which will probably form, and it is then added to the emulsion, well shaken and left for several days to ripen.

When thoroughly "ripened," the emulsion is filtered through a funnel containing a tuft of cotton wool.

The coated plates are bathed in distilled and finally in running water, until all greasiness disappears. The preservative is then applied and the plates dried for use.

Collodion Emulsion Suitable for Colour Sensitizing.*

1. Dissolve 50 grammes silver nitrate in 50 ccm. water (distilled), and add sufficient ammonia to get a clear solution, and 25 ccm. absolute alcohol.

2. Dissolve 32 grammes bromide of ammonium in 35 ccm. water distilled; add 50 ccm. alcohol, heat until dissolved.

Take a Winchester bottle, clean it well with sulphuric acid, and pour into this bottle 600 ccm. collodion 4 per cent., and add in the dark-room solution I., which must be perfectly cold. Some pyroxyline will separate, but re-dissolve after well shaking. A certain amount of silver nitrate remains however in suspension in the form of fine crystals.

We add now the warm bromide solution II. in small quantities, shaking well for about three minutes.

The emulsion is now precipitated with distilled water, washed and dried with alcohol.

The pellicle is put into 250 ccm. of alcohol and left for 24 hours.

After this period 150 ccm. of this alcohol replaced by 150 ccm. of fresh alcohol, in which 0·5 gr. of narcotin has been dissolved and 250 ccm. of ether are added. After three days the emulsion is diluted with 500 ccm. of ether-alcohol.

If the emulsion is required for the eosine silver bath process 5 ccm. of ethyl sulphuric acid are to be added.

Another very reliable formula is the following:—†

Sol. I.	Celloidin collodion, 4% ..	700 ccm.
Sol. II.	Silver nitrate	50 gramm.
	Ammonia	50 ccm.
	Add	
	Alcohol, 95%	100 ccm.

Dissolve. If not clear, add more ammonia.

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*Baron von Hübl's "Collodion Emulsion."

†Published by Baron Von Hübl in the "Atelier des Photographen."

If this solution crystallizes out add a few drops of distilled water.

Sol. III.	Bromide of ammonium ..	27 gramm.
	Water..................	40 ccm.

Heat this solution and add

Alcohol	100 ccm.
and	
Chloride of lithium solution (1 : 10 alcohol)......	15 ccm.

The chloride of lithium solution is made up as follows :—

Chloride of lithium......	10 gramm.
Distilled water	10 ccm.
Alcohol	90 „

After adding the chloride of lithium solution put the bottle containing solution III. into hot water.

Now mix solution II. with solution I. in the dark-room and shake well, and add in very small quantities the solution III., shaking well all the time. Now let the emulsion stand for 2 to 4 hours and pour a few drops on a glass plate and examine by transmitted light.

The emulsion must show an orange-red colour. If it is blue-grey in colour it will be of little use. The emulsion is precipitated in water in the usual way, washed and the water expelled with alcohol.

Dissolve the pellicle in

Alcohol	350 ccm.
Ether	400 „

Filter.

The materials necessary for the making of the collodion emulsion have to be of the very best quality in the first instance, and everything coming in contact with the emulsion must be chemically clean.

The sulphuric acid and bichromate of potassium cleaning solution, of which a formula is given on page 36, should be used, the bottles, measures, etc., are to be rinsed well under tap and freed from water by rinsing with alcohol.

4.—DEFECTS AND REMEDIES.

White spots are caused by dust, generally of organic origin.

These spots are also caused by dust in the substratum, and are very numerous in substratumed plates coated with ordinary emulsion. They are rarely met with in emulsions to which a simple aniline dye has been added, these are, however, present in emulsions sensitized with aniline silver compounds. See Fig. IV., Plate VIII.

The only remedy is a thorough cleaning of the dark-room, removal of unnecessary shelves and bottles, etc., which harbour dust.

An ideal dark-room for collodion emulsion work should be white-tiled like a dairy, so as to make the dust as conspicuous as possible, and invite greatest cleanliness. A zinc-lined floor would be preferable to the usual linoleum, and emptiness should be the principal feature of the room.

Black spots are caused by nitrate of silver, generally to be found in wet plate dark-rooms or slides or cameras.

They are also met with in the shape of *Comets* and other star-shaped spots, and require drastic measures. See Fig. IV., Plate VIII.

The re-varnishing and washing out of such dark slides is of little use, and new dark slides should be got.

We remember a case of a Levy screen having been used for wet plate work, and although well cleaned and polished, caused these black silver spots.

After washing the surface with a strong cyanide solution, the spots gradually disappeared.

The sensitizer " A," if standing for a few days, will, if not filtered, cause black spots. They are, however, perfectly round, and are never of the comet-shape.

Black streaks are caused by the diluted " A " sensitizer, with which the plate has been flowed and which runs

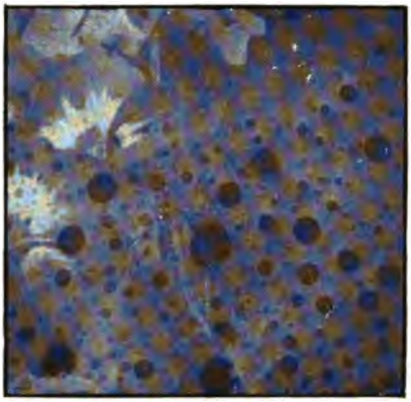

Fig. I.—Developing marks on a Collodion Emulsion Plate.

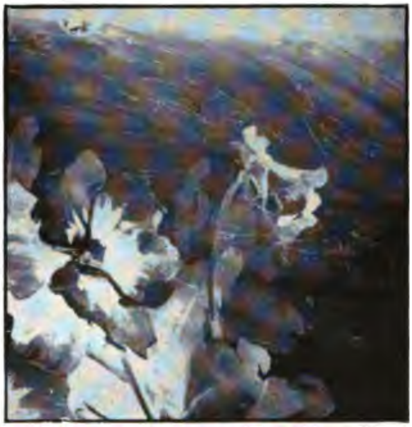

Fig. II.—Irregular markings due to insufficient cleaning of the glass. The thin white lines are scratches in the glass.

UNIV. OF

Plate VIII.

Fig. III.—Black streaks caused by " A " Sensitizer.

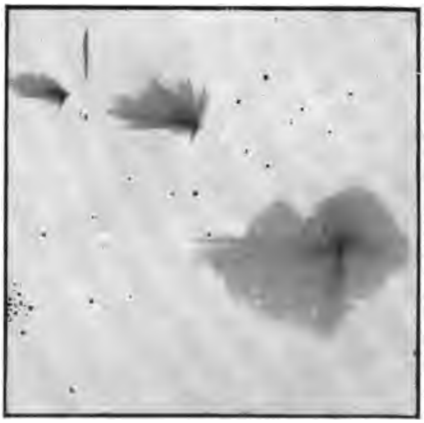

Fig. IV.—White and black spots and comets caused by Ordinary and Nitrate of Silver Dust.

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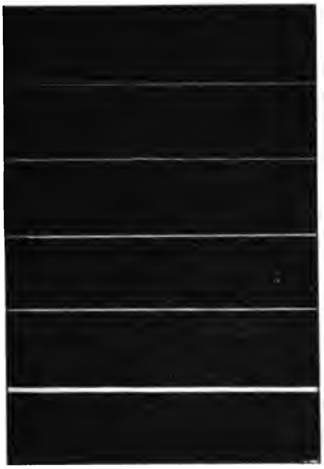

Fig. I.—Illustrates actual thickness of lines photographed.

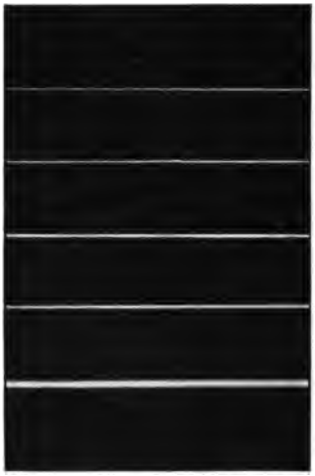

Fig. II.—Irradiation on a wet plate.

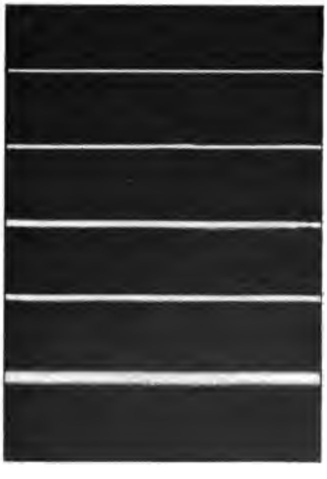

Fig. III.—Irradiation on a Fine Grain Dry Plate.

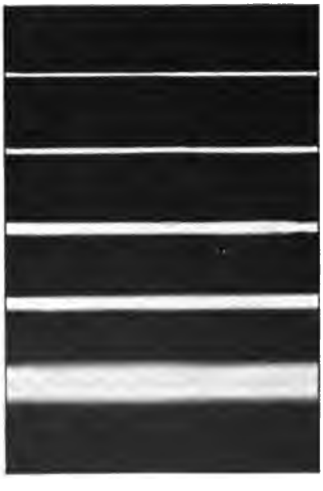

Fig. IV.—Irradiation on a Collodion Emulsion Plate.

down during exposure, and being somewhat convex-shaped, magnifies the dots and so really causes over-exposure in those particular parts of the plate. Being due to a repellent action of the sensitive surface, it is well to flow the plate several times and dry the metal clip in the dark slides on which the plate rests. See Fig. III., Plate VIII.

Irregular markings are caused by insufficient cleaning of the plates. Sometimes noticeable as polishing marks. A substratum may be used, but we always found it better to do without it, and be very careful in the cleaning, polishing and dusting of our plates. See Fig. I., Plate VII.

Fog, if not caused by unsafe dark-room light or excessive exposure to it, may be due to too high temperature. If eosine silver sensitizers are used the temperature of the solutions must be below 45°F.

The proper way of examining a half-tone emulsion negative is to view it against a dark background, and not against a powerful light.

Negatives correctly exposed always appear under-exposed in transmitted light, but in reflected light show distinctly a halo which surrounds a solid centre, and causes the so-called "joining up" of the high-lights.

Halation or irradiation is a defect which plays an important rôle in collodion emulsion work. To apply and utilize halation in trichromatic working methods has been the object of extensive research work, conducted by the photographic department of the Regent Street Polytechnic Institution, the results of which have been embodied in a paper read before the Royal Photographic Society, May 10th, 1904. By the courtesy of Mr. Howard Farmer, I am enabled to reprint some illustrations and parts of the lecture. It has been pointed out that "the vexatious uncertainties and failures in collodion emulsion colour work arise from irradiation, an effect, which, well studied and understood, instead of being a defect, becomes the chief optical adjustment for the attainment of reliable and uniform results."

The paper points out that "the optical principle employed in screen negative making is similar to the action which takes place if a card with an aperture be supported in front of a piece of sensitive paper and exposed to light in such a manner, that the greatest quantity of light reaches the paper opposite the centre of the hole, and a diminishing quantity in a radial direction from the centre, an extension, in fact of the ordinary principle of vignetting; its mode of application consists in the well-known adjustments of stop and screen distance, which, working in conjunction with one another, produce the necessary gradation in the size of the dots."

The paper, after pointing out the marked effects of irradiation in collodion emulsion, states: "These facts place at our disposal an entirely distinct system of screen negative making, for irradiation will alone translate pure tone into the most perfect gradation of dots. With the wet plate the action is slight and hardly noticeable with the ordinary exposures for screen negative making. With collodion emulsion, on the other hand, it is not only most marked, but takes full effect with the same exposure, which gives the dots with the ordinary system.

The operator, in endeavouring to obtain a screen negative by the application of the ordinary methods which he knows give perfect results with wet collodion, is dealing with a film of totally different character and with which *two* additional effects are operating. The first is that the range of gradation which produces black to white with the dyed collodion emulsion is very much less than is the case with wet collodion, about 1 : 8, as compared with 1 : 64; the second is the spreading due to irradiation. With most subjects, therefore, the high-lights simply clog up."

Messrs. H. Farmer and G. Symmons explain now, how by placing the screen in optical contact with the plate, the operator would make practical use of the irradiation defect and obtain a good negative, but that on account of the screen ruling being sealed between two glasses and the plate being wet, he will have to adopt the nearest approximation, by making the separation as small as is practical and employ with it a very small stop.

As the effect of halation, however, is more marked with one dye than it is with another, the irradiation method of making half-tone negatives with collodion emulsion may be varied, according to the degree of halation different emulsions are subject to. Collodion emulsion without the addition of colour sensitizers is almost free from this defect, and the usual stops and screen distances used for wet collodion need not be dispensed with. Collodion emulsion and Eosine are known to give very contrasty negatives, brilliant and free from halation. Canary Yellow, Rose Bengal, " A " sensitizer show similar properties. The latter, although an eoside of silver compound, is freed from excessive halation, to which it would otherwise be subject, by the presence of picrate of ammonia. The dyes Pinaverdol, Homocol, Orthochrom, Pinachrom, Katachrom, Ethyl Violet, Wool-black, Chlorophyll, and in particular Cyanine, produce a woolly dot in collodion emulsion negatives. This phenomenon may to a great extent be due to halation, but as all such sensitized emulsions give a considerably sharper dot before washing the plate, we believe that irradiation alone is not the only cause of the defect. As pointed out in another chapter, *viz.*, page 59, the unsharp dot may arise from vibrations of the air between screen and plate, due to the evaporation of the water which is present.

Dr. E Albert, a great authority on collodion emulsion, also studied this curious phenomenon and strongly supports this hypothesis.

It must further be remembered that thick emulsion films are less liable to irradiation than thin films, and that the presence of water in the solvents or excess of it in the sensitizers must increase halation. The writer introduced small quantities of non-sensitizing, but halation-preventing aniline dyes into the sensitized emulsion, as, for instance, Flavazine T, Brilliant Green, etc., and obtained good effects. In this case the collodion is stained without interfering with the colour sensitiveness of the bromide of silver molecule. Thiazol Yellow is also very effective in collodion emulsions sensitized with Ethyl Violet, the half-tone dots are sharper and larger stops may be used. Backing of the plates has been recommended, and the most suitable method is that with black paper soaked in glycerine and alcohol and squeegeed on to the back of the plate before coating with emulsion, see page 56.

In most cases we found it most practical to sensitize a rather slow and very hard-working emulsion with Ethyl Violet, and to add small quantities of Thiazol Yellow or Monobromofluorescinate of Sodium. Such emulsions do not require the excessive stopping down of the lens which is necessary with fast working Ethyl Violet emulsions. The speed of the emulsion, being greatly increased by the addition of Ethyl Violet, will be found high enough to suit the requirements of the process.

To decrease exposures by using highly sensitive emulsions is misapplied in this case, because the slight gain of time in making the exposures is dearly paid for by getting a woolly dot, which has no foundation to work upon, never gets density and causes more " solids " in the printing plate than desirable. The high-lights also do not close up, properly, the centre between the dots is veiled and as the connection between them does not permit of much reducing, when intensified, they close up completely, rendering the negative useless. But worst of all, the final failure can many times not be anticipated and so a great deal of time is wasted and eventually, a negative is produced which shows a quality very temper-trying to the man who has to print it. Slow-working emulsions are, however, quite fast enough, especially if the exposures are made with " flame carbons," which if burned in enclosed lamps on a high voltage, give a brilliant orange coloured light of high intensity and so shorten the exposures to about one-third of that necessary with ordinary carbons. The best carbons for the purpose are known by the name of " Triple

Cored Orange Flame Carbons." and are obtainable of dealers in electrical appliances. To avoid the changing of the carbons during the exposures and a great loss of time in waiting for the lamp to cool, a tri-colour enclosed arc lamp has been constructed, which carries two pairs of ordinary and flame carbons which can be switched on independently.

CONCLUSION.

In the foregoing chapters will be found an indication as to the position collodion emulsion holds at the time of writing. The wet plate will be chiefly used for line work and there production of black and white subjects in half-tone, in the first instance on account of superiority of results, in the second on account of expense and the disturbance to business routine, which may probably result through the introduction of a new process with which a great proportion of operators are not familiar.

The dry plate, and in particular the orthochromatic dry plate which has reached such a high point of excellence, will remain to offer the best working methods for out-door work, for portrait, landscape, and indirect tricolour reproduction in picture galleries.

Collodion emulsion will step in where the others fail, or prove to be too expensive. For direct three-colour half-tone work, the reproduction of paintings in monochrome, for ferrotype dry plates, lantern slides and transparencies, wood engraving, collodion emulsion will find no equal. In the hands of the intelligent operator, it will prove a reliable and a pliable process, for it will permit of no end of variations to suit certain requirements, but to the careless "slap dash" worker it will be a probable cause of his being visited by the most aggravating and apparently mysterious troubles he may ever dream of.

This chiefly accounts for the bad reputation collodion emulsion at one time enjoyed in certain quarters, and for the heartbreaking work of its re-introduction.

RECIPES.

DEVELOPERS FOR COLLODION EMULSION.

Glycin.

Dissolve
2½ ozs. of sodium sulphite
in
4 ozs. of water distilled (hot),
and add
1 oz. of glycin
and
5 ozs. of carbonate of potassium.

The order of mixing as stated above should be carefully followed.

The solution forms a thick paste, and will keep for years, if well stoppered. For use dilute :—

1 part of glycin paste with
12 parts of water.

This forms the usual developer.

Hydroquinone.

A.

Water, distilled	20 ozs.
Sulphite of sodium	10 ozs.
Carbonate of potash	8 ozs.

B.

Hydroquinone	1 oz.
Water, distilled	4 ozs.

C.

Ammonium bromide	1 oz.
Water, distilled	4 ozs.

Mix the three solutions and keep as stock. For use dilute 1 to 10.

Edinol and Hydroquinone.

A.	Water, distilled	200 parts
	Acetone sulphite (Bayer)	20 „
	Carbonate of potash	80 „

Add acetone sulphite *after* dissolving the potash.

B.	Hydroquinone	15 parts
	Alcohol	100 „
	Edinol	10 „
	Water, distilled	100 „

Edinol is dissolved separately and added to the rest after solution.

C.	Bromide of potash	10 parts
	Water, distilled	20 „

Take	100	parts	of solution	A.
	10	„	„	B.
	5—10	„	„	C.
and	1500	„	„	water .

The bromide of potassium can be dispensed with entirely. The developer works very clear and gives good gradation. If greater density is required use more hydroquinone.

Metol.

Water	10 ounces
Metol	75 grains
Sulphite of soda	1¼ ounces
Carbonate of soda	1¾ ounces
Bromide of potassium	10 grains

Dissolve metol before adding the sulphite.

For use take

1 part and dilute with
2 parts of water.

DEVELOPER FOR FERROTYPE PLATES.

A.

Sol. I.

Water, distilled	24 ounces
Sulphite of soda (specially pure) ..	10 „
Carbonate of potash (specially pure)	8 „
Ammonium bromide	1 ounce

Sol. II.

Hydroquinone	1 ounce
Water, distilled..................	4 ounces

Mix and label the solution A.

B.

Carbonate of potassium	6 ounces
Sodium sulphite	12 „
Glycin..........................	1 ounce
Water	20 ounces

Powder the sodium sulphite well and add the glycin after everything is dissolved.

Mix and label the solution B.

C.

Hypo	1 ounce
Water	10 ounces

For use take :—

3 drams of A
3 drams of B
9 drams of water
and 10-20 minims of solution C.

INTENSIFIERS FOR COLLODION EMULSION.

Nitrate of Lead.

Water, distilled	25 ounces
Ferricyanide of potassium	1 ounce
Nitrate of lead	1 „

Dissolve and filter.

The reduced and washed negative is left in the intensifier until yellow right through, washed, rinsed with .

Hydrochloric acid	½ ounce
Water	100 ounces

rinsed again under the tap and blackened with 3 per cent. solution of sodium sulphide, rinsed again under the tap, cleared with the hydrochloric acid solution, rinsed again under the tap, gummed and dried.

Bichloride of Mercury.

Sol. I.

Water	30 ozs.
Common salt	60 grains
Bichloride of mercury	60 „
Hydrochloric acid	5 minims

The plate is well washed and drained after the fixing, and bleached in this solution. Then well washed again and flowed with

Sol. II.

Liquid ammonia	3 drams
Water, distilled	4 oz.

Bromide of Copper.

Sol. I.

Bromide of potassium	2 ounces
Sulphate of copper	1½ „
Water	68 „
Nitric acid, pure	35 minims

Sol. II.

Nitrate of silver	1½ ounces
Water, distilled	100 „

REDUCERS FOR COLLODION EMULSION.

Farmer's.

(To be used before intensification with lead).

(A)	Ferricyanide of potassium	1 ounce
	Water	25 ounces

(B)	Hypo	1 ounce
	Water	10 ounces

For use mix

(A)	1 ounce
(B)	2 ounces
Water	10 „

Iodine and Cyanide.

Iodine	40 grains
Potassium iodide	80 „
Water	20 ozs.

Bleach the negative with this solution, rinse under the tap and apply a weak solution of cyanide of potassium until the shadow dots are of the required size. Wash and blacken with a solution of sodium sulphide. Wash and varnish with

VARNISH FOR COLLODION EMULSION.

Gum arabic	4 ozs.
Water	40 ozs.
Carbolic acid	35 minims

GLASS-CLEANING SOLUTION.

Bichromate of potassium	2 ozs.
Sulphuric acid	3 „
Water	25 „

Rinse under the tap and polish with an alcoholic solution of caustic potash or iodine, and finally polish with papier Joseph or with a clean pad of linen charged with a few drops of alcohol and ammonia.

SUBSTRATA.

Indiarubber.

Indiraubber (best Para)	1 part
Anhydrous benzole or (chloroform)	500 parts

Albumen.

Water	80 ozs.
Albumen	1 oz.
Ammonia	1 minim

Gelatine.

1—Gelatine	50 grains
Acetic acid	½ oz.

The gelatine is warmed until dissolved.

2—Water	½ oz.
Chrome alum	10 grains

Take 2½ parts of No. 1; 1 part of No. 2; methylated spirits, 70 parts, and filter.

PRESERVATIVE FOR COLLODION EMULSION.

Tannin	500 grains
Gallic acid	200 „
Grape sugar	200 „
Strong acetic acid	10 oz.

PLATE-BACKING SOLUTION FOR COLLODION EMULSION.

Glycerine	1 part
Alcohol	2 parts
Water	2 „

In this solution soak black paper which is used for wrapping up dry plates until pliable, and squeegee on to the back of the plates before coating.

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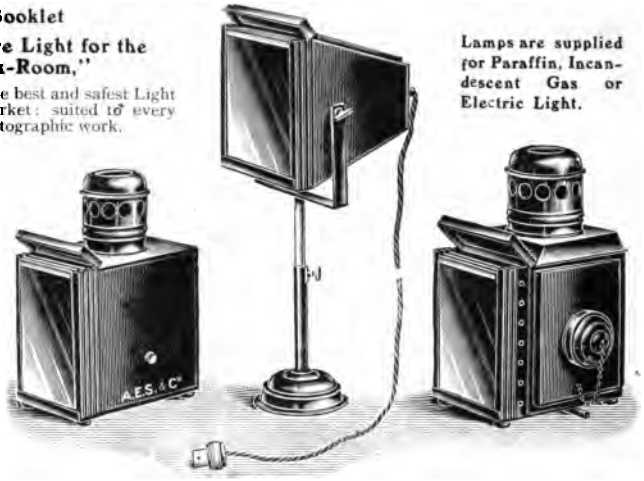

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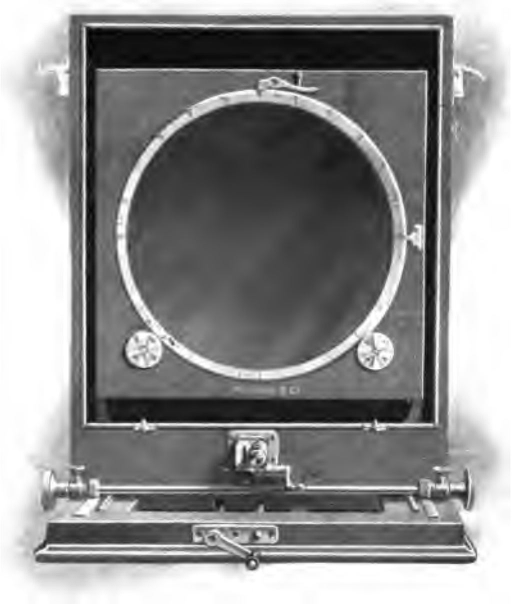

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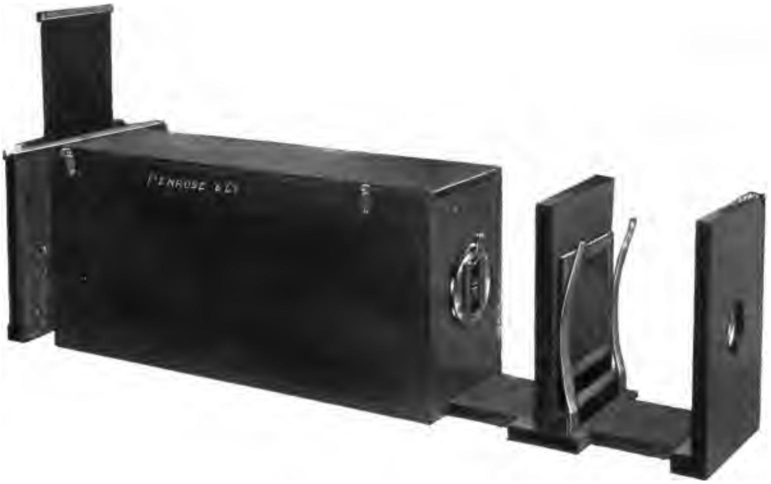

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Invaluable for all kinds of Spectroscopic Tests. Can be used for testing the colour sensitiveness of plates, adjusting liquid colour filters, testing dry filters, determining relative exposures, and generally for studying the principles of spectroscopic work.

☞ The camera is of fixed focus and always ready for use. Every camera tested before being sent out. Daylight, incandescent gas, or electric light can be used for making the exposures.

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This addition is strongly recommended

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Eosine, blue shade
Eosine, yellow shade
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Fast Green, B (Bayer)
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The Safe Light Lantern.
For Incandescent Electric Light. Price **12/6**
(Without Safe Light or Lamp).

The Spectra Lamp.
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Price **10/6**, including Lamp.

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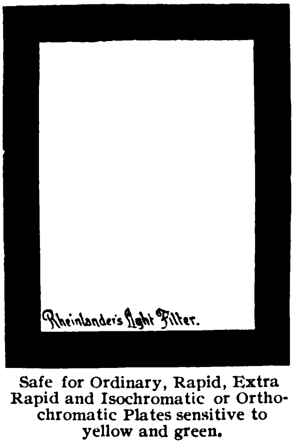
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For perfectly safe illumination of the Dark-Room.

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For Interiors, Groups, Portraits, Machinery, Trade Objects.
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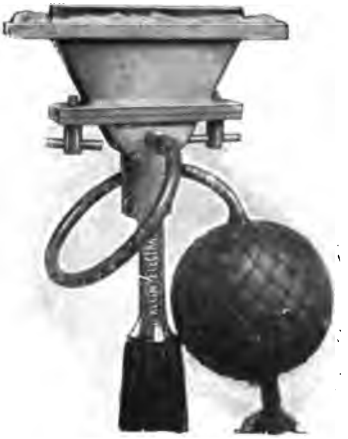

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ADVANTAGES : *Quick Ignition. Wide-Spreading Fan-Shaped Flame. Great Intensity. Easy to Charge. Simple and Compact.*

Price of the " Electra " Flash Lamp, in aluminium, complete with Double Ball and Tube of best rubber **15/6**

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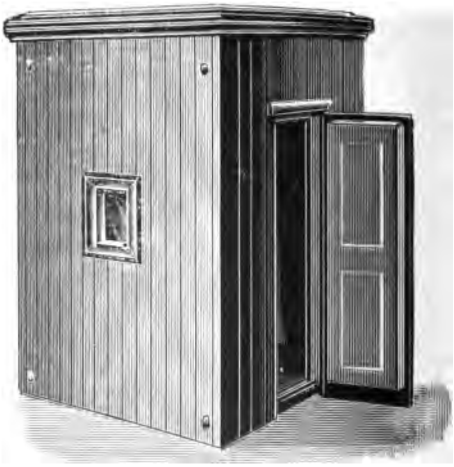

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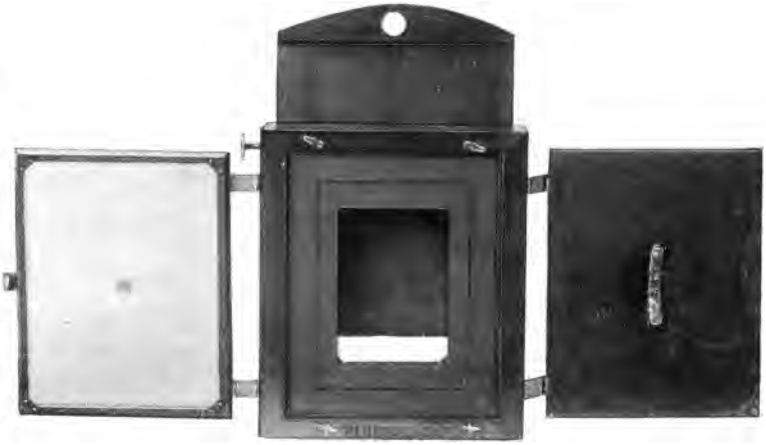

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